SOME SYNTHETIC PATHWAYS INVOLVING TETRACARBONYLCOBALTATE (1-)

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Declaration

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Abstract

The aim of this work was to assess the viability and limitations of certain reactions of the tetracarbonylcobaltate (1-) anion with organic halides as steps in some synthetic pathways. Primarily, the work was concerned with attempts to extend the formation of dialkyl ketones from alkyl halides and carbon monoxide to the formation of cyclic ketones from α,ω-dihalides and carbon monoxide.

During the course of the work, the fortuitous discovery was made that the halide anion catalyses the formation of tetracarbonylcobaltate (1-) from neutral cobalt carbonyls in complexing-ethereal solvents. It was decided to study the factors governing halide induced valence disproportionation and to attempt to extend this reaction to inert solvent systems: The consequences of performing subsequent synthetic steps involving tetracarbonylcobaltate (1-) derivatives in hydrocarbon media and in complexing-ether solutions were compared.

The valence disproportionation of neutral cobalt carbonyls to tetracarbonylcobaltate (1-) and a divalent cobalt species in complexing ethers was found to be catalysed by soluble chlorides, bromides and iodides. The halide catalysed valence disproportionation reaction in complexing ethers was found not to obey any simple rate law. Indeed, in some cases, the concentrations of octacarbonyldicobalt or dodecacarbonyltetracobalt were found to exhibit damped oscillatory behaviour. A tentative explanation of this behaviour is advanced in terms of the valence symproportionation

of divalent cobalt and tetracarbonylcobaltate (1-) to neutral cobalt carbonyl and of catalyst poisoning that takes the form of complexation of free halide to divalent cobalt.

Halide induced valence disproportionation of cobalt carbonyls was extended to hydrocarbon solvent systems by use of suitably soluble halides. Where a large excess of tetra-n-butylammonium iodide is present, octacarbonyldicobalt is disproportionated in toluene according to first order kinetics. The salt bis-[(dicyclohexyl-18-crown-6)potassium] tetrahalocobaltate (halo = chloro or bromo) and [(dicyclohexyl-18-crown-6)cobalt (II)] tetrachlorocobaltate bring about the valence disproportionation only very slowly in hydrocarbon solvents. These facts appear to confirm that free halide is the true catalyst and that the tetrahalocobaltate anion is itself either inferior or totally ineffective.

Some salts of tetracarbonylcobaltate (1-) are soluble in hydrocarbon solvents. Synthetic pathways involving the anion may, therefore, be carried out in the complete absence of bases.

Tetracarbonylcobaltate (1-) reacts with acyl halides in hydrocarbon media without reaction between the halide and the solvent: We have found that such a side-reaction partly obstructs the desired reaction in ethereal solutions. The yield of ketone formed from the acyl halide by formation and subsequent thermal decomposition of the acyl cobalt tetracarbonyl intermediate is thus enhanced in hydrocarbons.

Attempts to form cyclic ketones by intramolecular binuclear

elimination from 1,8-octanedioic acid bis-(tetracarbonylcobaltate) and 1,4-butanedioic acid bis-(tetracarbonylcobaltate) were unsuccessful. The fate of the hydrocarbon backbone of these molecules remains unknown. At high temperatures (161 °C), 1,7-octadiene is a product of the thermal degradation of 1,10-decandioic acid bis-(tetracarbonylcobaltate).

o-Bis-(halomethyl)-arenes react to give, in some cases, very good yields of the five membered ring ketone resulting from carbonylation and cyclisation.

The nature of the observed organocobalt intermediate in these reactions depends strongly on the properties of the arene: Thus α,α'-dibromo-o-xylene gives a (monohaptoalkyl)-cobalt tetracarbonyl, 2,3-bis-(bromomethyl)-naphthalene gives a (trihaptoallylic)-cobalt tricarbonyl species and 2,3-bis-(bromomethyl)-quinoxaline gives a metallacyclic species in which nitrogen is co-ordinated to cobalt.

The rearrangements suffered by the (presumably) initially formed (monohaptoalkyl)-cobalt tetracarbonyl affect the final yield of carbonylated product: Thus the yield of the novel species, 1,3-dihydro-(2H)-benz-[f]-inden-2-one obtainable by this method appears to be substantially lower than that obtainable for indan-2-one. No ketone was detected following the reaction of 2,3-bis-(bromomethyl)-quinoxaline with tetracarbonylcobaltate (1-)

The cobalt carbonyl derivatives formed from (α-haloalkyl)-arenes were found to be subject to cobalt-carbon bond homolysis. Decomposition of the intermediates by this step explains the imperfect yields of ketone obtained by this route.

The tendency for homolysis in the 2,3-bis-(bromomethyl)-quinoxaline derivative appears to be anomalously great.

A (trihaptoallylic)-cobalt tricarbonyl species is formed by the reaction of tetracarbonylcobaltate with z,z-cis,-cis-3,7-dibromocyclo-octa-1,5-diene. This intermediate decomposes in benzene to give bicyclo [5.1.0] octa-2,5-diene. No evidence of carbonylated products was found.

2-Phenylpropionyltetracarbonylcobalt (I) (hydratropyltetracarbonylcobalt) is produced following apparently ready carbonylation of 1-phenylethyltetracarbonylcobalt (I); the product of the attack by tetracarbonylcobaltate (1-) on (α-bromoethyl)-benzene.

Hydratropyltetracarbonylcobalt (I) isomerises over a period of several hours in tetrahydrofuran at room temperature to give 3-phenylpropionyltetracarbonylcobalt (I) (hydrocinnamyltetracarbonylcobalt (I)). The isomerisation reaction is slow compared with attack by a strongly nucleophilic, unhindered base, such as the methoxide anion. Thus methyl hydratropate may be formed in high yield. Adding aniline to a solution of hydratropyltetracarbonylcobalt (I), however, results in the slow formation of hydrocinnamanilide.

Mixtures of hydratropanilide and hydrocinnamanilide were produced by performing the same reaction in benzene, and by attack by the anilide anion on the organocobalt intermediates.

Abbreviations

a) units

atm.	atmosphere
^{o}C	degree Celsius
D	Debye unit
g	gram
hr.	hour
Hz	Hertz
J	joule
l	litre
m	metre
M	molar ($mol.l^{-1}$)
min.	minute
mol.	mole
sec.	second
δ	chemical shift in parts per million downfield of t.m.s. (in n.m.r.)

b) multipliers

c	centi
k	kilo
M	mega
m	milli
n	nano

c) Spectral characteristics

m		medium
max.		maximum
s		strong
sh		shoulder
vs		very strong
vw		very weak
w		weak
λ	represents	wavelength
ν	indicates	a stretching mode of vibration

d) General

cf	compare
conc.	concentration, concentrated
ct.	contrast
g.l.c.	gas-liquid chromatography
HCBD	hexachlorobutadiene
i.r.	infrared (spectrum or spectroscopy)
$\log_{10}$	logarithm to the base, ten
ln	natural logarithm
M.Pt.	melting point
n	normal
n.m.r.	nuclear magnetic resonance (spectrum or spectroscopy)
R_f	distance travelled by a band divided by the distance travelled by the solvent front (in t.l.c.)

R.T.	Room temperature
soln.	solution
t.	tertiary
t.l.c.	thin layer chromatography
t.m.s.	tetramethylsilane

Other abbreviations are explained in the text.

CHAPTER ONE

INTRODUCTION

CHAPTER ONE : INTRODUCTION

SECTION ONE : COBALT

a) Historical

European metallurgists of the middle ages were frequently frustrated in their attempts to produce copper and some other metals from their ores. Either an apparently rich ore would yield no metal on application of the usual treatments, or the metal would be contaminated by an intractable residue. In some cases extremely toxic vapours arose during treatment of these ores. Obviously, arcane forces were involved, and the metallurgists blamed Kobold, the mine-dwelling goblin of Nordic mythology.

This story may or may not be true, but when, in the early eighteenth century, it was realised that the false ores and residues were in fact compounds (arsenides and arsenosulphides) of a distinct metal, the name, Kobalt was applied. (Berthelot[1] suggests an alternative etymology. The word, κοβαθία , appears in the writings of the ancient Greek alchemist, Olympiodoros, in circumstances which suggest that this may have been cobalt). The word, cobalt, entered the English language in the year 1728[2]. It can be assumed that the general recognition of cobalt as an element shortly predated this.

As far as the scientific community was concerned, cobalt was first identified as a distinct metal by the Swedish chemi eorg Brandt in a dissertation presented in 1739[3]. Brandt may also have been first to isolate the metal[4]. Even then, the existence of elemental cobalt was doubted. Brandt's work was repeated and finally verified by Bergman, another Swede, in 1780[5].

Despite this comparatively late recognition (for a common workable

metal), technology involving cobalt was as ancient as that of many other metals. For example, cobaltous materials have been employed in the manufacture of blue glass and glazes for several millenia[6].

Cobalt was present at the birth of modern chemistry. It is mentioned by Lavoisier as an 'oxydable and acidifiable simple metallic body'[7]. Berzelius included cobalt in his 'Comparative Table of the Specific Weights of Elementary Bodies'[8]. He ascribed the weight of the element as 100/27.3 times that of oxygen. (Taking oxygen = 16, this is 58.61 which compares very well with the modern value of 58.93).

Werner used the cis-trans isomerisation of dihalo-bis-(ethylenediamine)-cobalt (III) halides to illustrate his idea of (in this case, octahedral) co-ordination of ligands to metal ions[9]. Thus, cobalt can be said to have played a prime rôle in the genesis of modern inorganic chemistry.

The general importance of cobalt in the inorganic chemistry of the late nineteenth and early twentieth centuries is illustrated by the penchant of chemists of the time (and later) for naming any transition metal complex by the colour of the analogous cobalt species.

b) Descriptive

The most commonly encountered form of cobalt is the red-pink hexaquacobalt (II) ion.

The electronic structure of divalent cobalt is $[Ar]\ 4s^0 3d^7$. It has been found that almost every octahedral cobalt (II) species

contains three unpaired electrons, and thus, the high spin configuration illustrated in figure 1 can be taken to prevail.

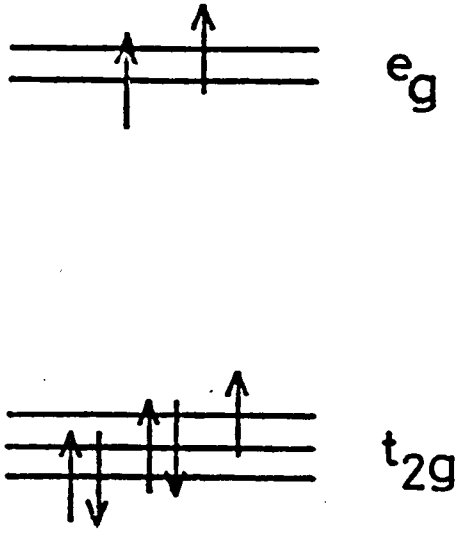


Figure 1. The high spin configuration in octahedral cobalt (II) species.

The unsymmetrical occupation of the t_{2g} levels implies a high orbital contribution to paramagnetism. This is borne out by the fact that the measured magnetic moments of octahedral divalent cobalt species are well in excess of the calculated spin-only values.

Application of the Russel-Saunders scheme to a d^7 system produces a ^4F ground state with one other spin quartet state, ^4P, at higher energy. The ^4F state is split into a $^4T_1$ state (the $t_{2g}^5 e_g^2$ configuration) which becomes the ground state, a $^4T_2$ state and a $^4A_2$ state under the influence of an octahedral ligand field. The orbital degeneracy of the ^4P is not lifted on application of an octahedral electrostatic field. The energy of the $^4T_1(F) \longrightarrow {}^4T_2$ transition means that light outwith the visible region of the spectrum is required to bring about the excitation. The band due to $^4T_1 \longrightarrow {}^4A_2$ is vanishingly weak[10a], and thus, the pink colour of hexaquacobalt (II) is attributable solely to the $^4T_1(F) \longrightarrow {}^4T_1(P)$

transition, which occurs at about 515 nm.

The familiar 'cobalt blue' colour arises from the visible region absorption of tetrahedral cobalt (II) species. The ^4F Russel-Saunders ground state of the d^7 system is split on the application of a tetrahedral ligand field into a $^4A_2$ state (the $e^4t_2^3$ configuration illustrated in figure 2) which is the ground state, a $^4T_2$ and a $^4T_1$ state. The ^4P state remains triply orbitally degenerate.

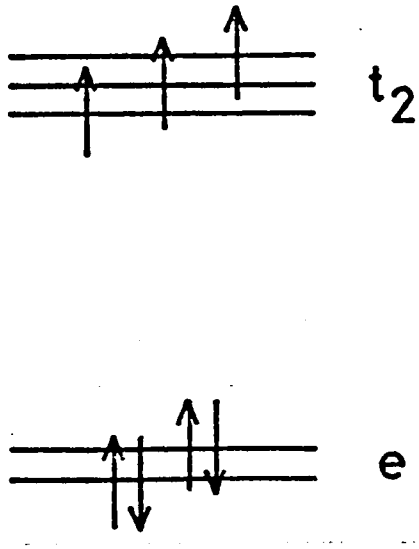


Figure 2: The ground state electronic configuration in tetrahedral divalent cobalt.

The $^4A_2 \longrightarrow {}^4T_1(P)$ transition requires energy which can be supplied by light in the visible spectrum (usually towards the red end). The visible region absorption of tetrahedral cobalt (II) is extremely intense compared with that of the centrosymmetric octahedral cobalt (II).

Since the ground state of tetrahedral cobalt (II) is orbitally non-degenerate, there is no inherent orbital contribution to paramagnetism. In real systems, however, substantial spin-orbit coupling mixes degenerate states of higher energy with the ground

state, and gives rise to orbital paramagnetism.

The tetrahedral and octahedral configurations are readily interconvertible. Where different ligands of similar spectrochemical strength are present, small changes in concentration, or in other conditions, can bring about the change. Heating hexaquacobalt(II) dichloride in the presence of a large excess of sodium chloride produces an intense blue solution.

Cobalt is also commonly encountered in its trivalent state, particularly when complexed by nitrogen bases.

Cobalt can be found in lower valence states when complexed by π- accepting ligands (vide infra). The $d^8 Co^I$ system is known to form trigonal bipyramidal complexes, although other co-ordination numbers and geometries are known where ligands impose constraints. Cobalt (0) and Cobalt (1-) are usually found in tetrahedral environments[10b].

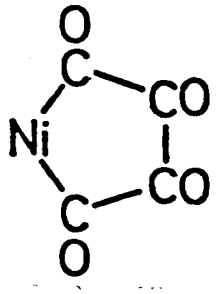
SECTION TWO : METAL CARBONYLS

a) Historical

In 1868, Schützenberger obtained a series of platinum chlorocarbonyls on passing a mixture of chlorine and carbon monoxide over the heated metal[11]. Despite extensive characterisation of the products and description of their properties, little interest seems to have been paid to Schützenberger's yellow crystals.

Twenty years elapsed between the discovery of the first metal carbonyl and the appearance of Ludwig Mond's paper, 'The Action of Carbon Monoxide on Nickel'[12]. The rapid development of metal carbonyl chemistry in the twenty years following the appearance of

Mond's paper can be appreciated from a paper published (post - humously) by Mond in 1910[13]. This paper describes the properties of eight metal carbonyls. Mond also expressed dissatisfaction with the proposed ring structure (e.g.(I)) of metal carbonyls. (Schützenberger had suggested metallacyclic structures for his carbonyls.) The tetrahedral structure of tetracarbonylnickel was not suggested until 1932[14].



(I)

It was perhaps the commercial viability of the Mond process for the purification of Nickel that encouraged interest in metal carbonyl chemistry in the first few decades of this century.

Sporadic discovery of new metal carbonyl systems occurred between 1910 and 1930.

Walter Hieber, with his paper on the reactions and derivatives of iron carbonyls[15] in 1928 began an immense study on metal carbonyls. Hieber was largely responsible for the construction of the background of fact against which the unifying theories of metal carbonyl chemistry have been drawn. Some relevant points of Hieber's voluminous works are listed below.

During forty years of research[16,17] Hieber discovered several metal carbonyl systems including the hydrocarbonyls of cobalt[18] and iron[19]. Hieber was able to show that some metal carbonyls are reduced by hydroxylic bases[20]. Reaction scheme (1) illustrates the

reaction of hydroxyl with pentacarbonyliron:

$$Fe(CO)_5 + 4\ OH^- \longrightarrow [Fe(CO)_4]^{2-} + CO_3^{2-} + 2H_2O \quad \text{——— (1)}$$

The reactions of oxygen bases (e.g. ethers) and nitrogen bases (amines) [21] with metal carbonyls were studied as were Reppe's reactions of phosphines and phosphites with metal carbonyls[23]. The relative propensities of the various metals, and of the various bases involved to react by a substitution pathway, e.g. (2), or by a valence disproportionation pathway, e.g. (3), were investigated.

$$Co_2(CO)_8 + 2PR_3 \longrightarrow (Co(CO)_3PR_3)_2 + 2CO \quad \text{——— (2)}$$

$$3Mn_2(CO)_{10} + 12C_6H_5N \text{ —— } 2[Mn(C_6H_5N)_6][Mn(CO)_5]_2 + 10\ CO \text{ —(3)}$$

Hieber was also involved in the earliest attempts to synthesize alkyl metal carbonyls, which he had believed to exist as early as 1935[24]. His report of alkylpentacarbonylmanganese(I)[25] and that, independently published by Closson, Kozikowski and Coffield[26] represented the first successful syntheses of these species.

It was with the discovery of compounds containing metal to carbon σ-bonds that metal carbonyls entered the main stream of organometallic chemistry. The tide of work carried out on metal carbonyl alkyls and acyls in the late 1950's and early 1960's testify to the great contribution made by metal carbonyl chemistry to the (then) infant branch of the subject.

Work of a more general, and a more empirical nature went on in parallel with that of the earlier work of Hieber. The stimulus for this work was the importance of metal carbonyls in catalysis. Sabatier, whose nickel catalysed hydrogenation of unsaturated hydrocarbons[27] virtually initiated the study of heterogeneous catalysis is quoted[28] as having said that his interest in the action

of nickel on unsaturated materials was provoked by Mond's discovery of nickel carbonyl.

Since carbon monoxide and hydrogen (synthesis gas) were readily available from coal, various syntheses involving these gases over metal catalysts were commercially attractive.

The first industrial scale process which probably involved metal carbonyls were the high pressure, high temperature reactions between carbon monoxide and hydrogen and between carbon monoxide and methane. These reactions gave hydrocarbons, alcohols, aldehydes, ketones or acids depending on the conditions[29].

Fischer and Tropsch[30] in 1926 discovered that carbon monoxide and hydrogen reacted over iron and cobalt catalysts to form alkanes, from which synthetic fuels could be produced. This, of course, stimulated great interest, and in the course of the ensuing work, the presence of oxygen-containing compounds in the product mixtures was noted[31].

It was discovered in 1930, that the reaction between ethylene, carbon monoxide and hydrogen over a cobalt-copper-manganese oxide catalyst gave oxygen containing products[32]. These were identified by Roelen as propionaldehyde and diethyl ketone. By modifying the conditions of the reaction, Roelen was able to develop the hydroformylation of olefins[33] into an industrially viable process. (The OXO process.)

The study of the hydroformylation reaction led to important developments in synthesis in the early 1950's. Reppe discovered the hydrocarboxylation of olefins[34] and acetylenes[35]. This line of work also led Reppe to discover the important metal halide/nickel carbonyl catalysed carbonylation of methanol[36]. Wender, Friedel and Orchin

discovered the cobalt carbonyl catalysed 'homologation' of methanol to ethanol (a reaction whose mechanism is not yet understood) in 1951[37]. Berg and Assinger discovered the isomerisation of olefins by Fischer Tropsch catalysts in 1955[38].

All of these processes, and the hydroformylation reaction itself have found significant industrial application.

It is not surprising that such a fertile source of viable industrial processes attracted interest. In order that information could be derived about factors which are important in determining catalytic activity, the metal carbonyls were more avidly studied.

With the discovery of alkyl metal carbonyls[25,26] the two strands of development met. In 1960, Heck and Breslow[39] presented a convincing mechanism for the hydroformylation of olefins involving alkyl cobalt intermediates. Comparatively recently, direct proof of the presence of alkyl cobalt carbonyl species in hydroformylation reaction mixtures has been derived from in situ high pressure infrared studies[40].

Success in this area led to attempts to extend the interpretation of other catalytic reactions in terms of metal alkyl intermediates. It was reasoned that a large molecular metal cluster should have several of the properties of a metal surface. Metal carbonyls have been found to be amenable to cluster formation, and so much of the interest in metal clusters has been focussed on these systems. Since the proposed mechanisms of heterogeneous catalysis have been called into doubt[41] by the presence of an active carbonaceous overlayer on metal catalyst surfaces[42], the hopes of drawing greater analogies between homogeneous and heterogeneous catalysis have been

damaged (though not entirely dashed[43]).

Homonuclear and internuclear metal carbonyl clusters continue to be of interest, however, for the information they yield on the nature of such items of interest as metal - metal bonding and delocalised orbitals[44]. A considerable amount of work continues to be invested in this area of research[45].

b) Descriptive

A schematic molecular orbital diagram for carbon monoxide is illustrated in figure 3. The 1σ, 2σ, 3σ and 4σ molecular orbitals are essentially (not entirely) centred on one or other of the atoms: for example, $1\sigma_{co}$ is largely composed of the $1s_o$ atomic orbital.

The $5\sigma_{co}$ orbital lies, to a large extent, on the side of

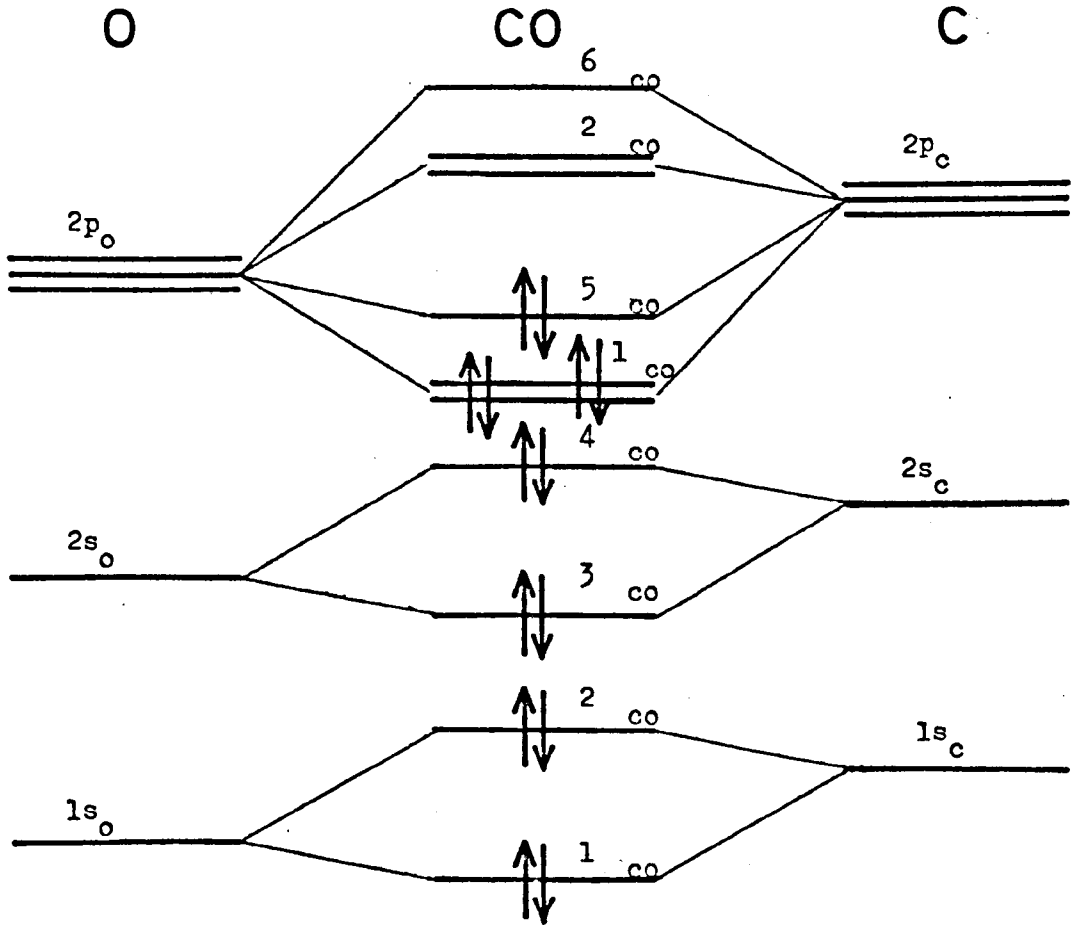


Figure 3: A molecular orbital diagram for carbon monoxide (adapted from Karplus and Porter[46])

carbon away from oxygen. When filled, this orbital approximates to a lone pair on the carbon. (Since greater weighting of the other filled orbitals lies towards the more electronegative oxygen atom, carbon monoxide is not strongly dipolar: 0.112 $\pm$ 0.01 D[47]). It is with this lone pair that carbon monoxide co-ordinates to metals.

Although mixing with other levels is serious, for the purposes of this discussion the $1\pi_{co}$ level can be considered to be the C - O π-bonding orbital. The $2\pi_{co}$ level, effectively a π^* antibonding orbital is centred more heavily on carbon than on oxygen, but with its 'centre of gravity' lying between the two atoms[48]. (Theoretical treatments[48] have been found to be at variance with experimental determinations[49] of the effect on the molecular dipole moment of occupying $2\pi_{co}$.) Occupation of this antibonding orbital should weaken the CO bond. A schematic representation of the $2\pi_{co}$ orbital is shown in figure 4.

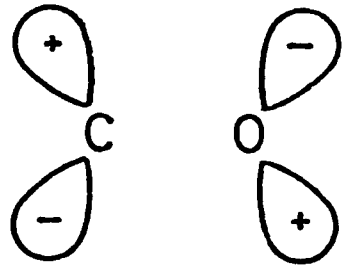


Figure 4: The $2\pi_{co}$ orbital
(The signs represent the phase of the wavefunction.)

The π-acceptor theory[50] states that a ligand with empty orbitals of suitable symmetry and of accessible energy can receive electron density from the filled d-orbitals of the metal to which it is bound. It can be seen from figure 4 that the 2π orbital of carbon monoxide is of suitable symmetry to bond with a metal d-orbital. A mass of observed

facts are consistent with 'back donation' taking place in metal carbonyls. A model of the system is illustrated in figure 5 in terms of the interactions between an unfilled metal hybrid orbital

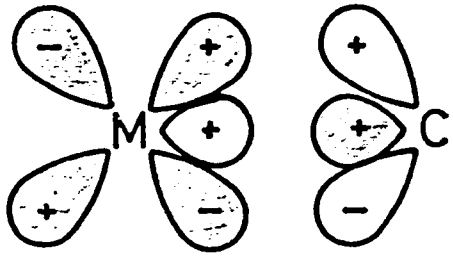


Figure 5: The σ and π interactions between a metal and a carbonyl group

and the $5\sigma_{co}$ orbital and between a filled metal orbital and the $2\pi_{co}$ orbital.

An idealised, qualitative molecular orbital diagram for metal hexacarbonyls involving the $2\pi_{co}$ orbitals has been proposed by Gray and Beach[51]. An adapted version of this scheme is illustrated in figure 6.

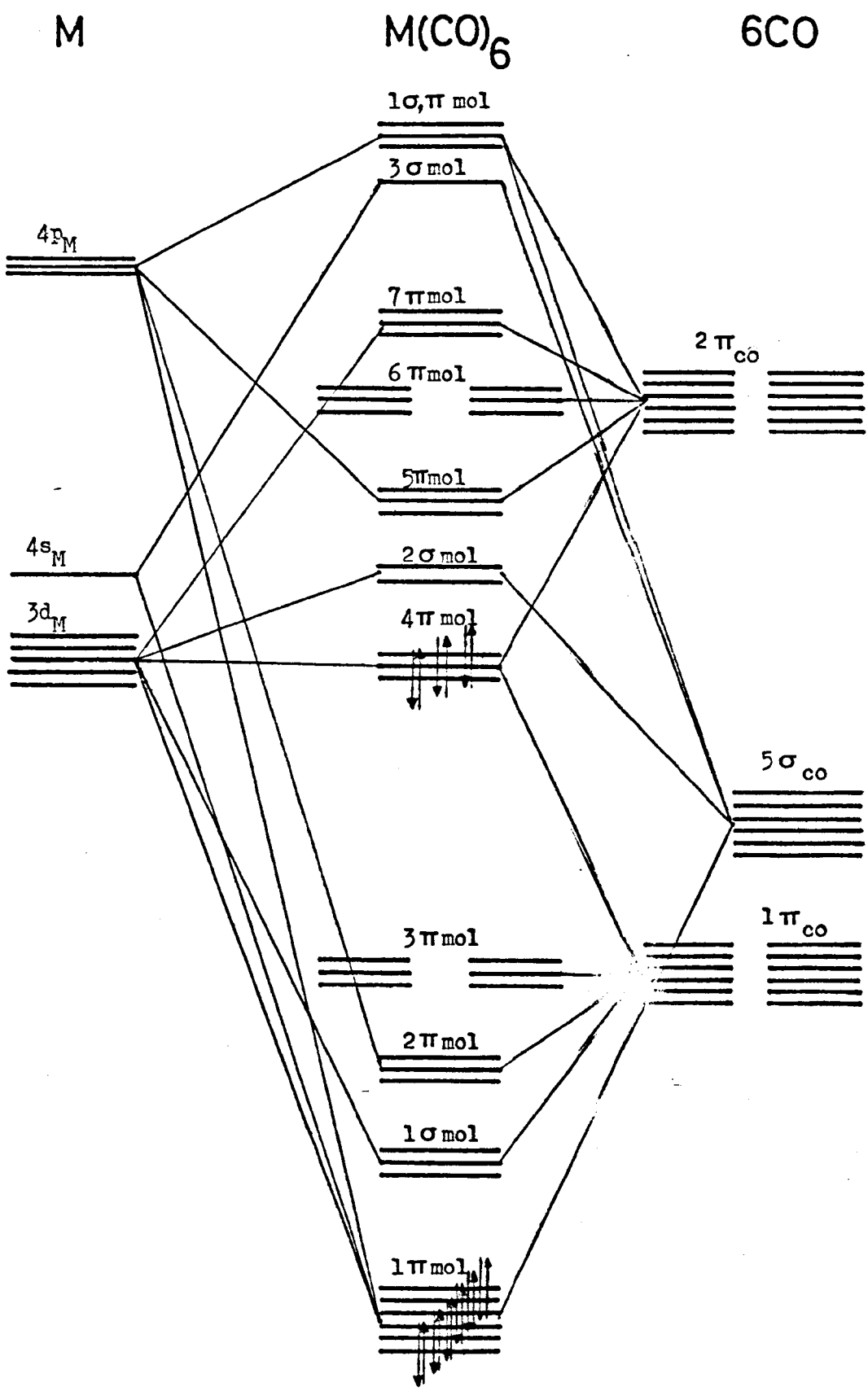


Figure 6

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In this representation, the a_{1g}, e_g and t_{1u} molecular orbitals comprising the $1\sigma_{mol}$ level are envisaged to be octahedrally hybridised to give the 6 metal-ligand σ-bonding interactions. The $1\pi_{mol}$, $2\pi_{mol}$ and $3\pi_{mol}$ levels remain, to all intents the $1\pi_{co}$ bonding orbitals. The $4\pi_{mol}$ level contains the $2\pi_{co} - 3d_m$ bonding interaction.

The destinations of the electrons from six carbonyl lone pairs and from the valence orbitals of a metal with six valence electrons are indicated in figure 6. (The electrons in the carbon-oxygen π-bonds have been omitted for clarity.) It can be seen that eighteen is exactly the number of electrons required to fill the six σ and three π bonding orbitals proposed by this molecular orbital scheme. It is commonly found that stable complexes of transition metals with π-accepting ligands have eighteen electrons involved in metal-ligand bonding[52].

Thus, zerovalent chromium might be expected to form a stable octahedral hexacarbonyl, with a formal metal-carbon bond order of 1.5 (since six metal-carbon bonds share the triplet of $4\pi_{mol}$ orbitals). Cotton and Wing[53] have related metal-carbon bond lengths to the proposed bond order for a number of molybdenum carbonyl compounds. They have taken the observed metal-carbon bond length in molybdenum hexacarbonyl to infer a bond order of 1.5. In qualitative terms, the molecular orbital diagram for hexacarbonylmolybdenum would be expected to be similar to that for hexacarbonylchromium. Analogies can also be drawn with the electronic structures of the hexacarbonylmanganese(I)monocation and the hexacarbonylvanadate(1-) anion, both of which are known[54,55].

It is conceptually difficult to extend the above treatment to achieve satisfactory molecular orbital descriptions of carbonyls of other geometries. It is possible to extend the diagram suggested by Cotton and Wilkinson (10b) for tetrahedral complexes to an eighteen electron tetrahedral tetracarbonyl, such as tetracarbonylcobaltate(1-). Such a diagram would account satisfactorily for such properties as the observed diamagnetism of the anion[23]. The picture does, however, present something of an embarrassment of riches, since it suggests that four ligand-metal bonds share five π-bonding orbitals. This indicates a metal-carbon bond order of 2.2 (cf. the spectroscopically estimated value of 1.89[56]).

A molecular orbital diagram for tetracarbonylcobaltate(1-) has appeared[57]. This does not show direct $3d_m - 2\pi_{co}$ bonding, and has been used only to give a conceptual starting point to describe the ^{59}Co n.m.r. of the anion which does show evidence of considerable $3d_m - 2\pi_{co}$ bonding.

A great deal of indirect evidence has been accumulated in support of the π-acid theory. The most convincing of this is the determination of the crystal structures of several carbonyls in which the metal carbon bonds have been shown to be substantially shorter than the sums of the covalent radii of the bonded metal and carbon atoms[e.g.53].

Recently, an electron density map of hexacarbonylchromium was derived by X-ray and neutron diffraction[58]. This shows occupancy of the $2\pi_{co}$ orbitals of 0.3 ± 0.1 electrons per carbonyl group. This constitutes direct evidence for the existence of metal carbonyl π-bonding.

Metal to carbon π-donation has significant consequences for the infrared spectra of transition metal carbonyls. Stretching a C-O bond decreases the carbon-oxygen antibonding interaction, thereby lowering the energy of the $2\pi_{co}$ level. This will increase the involvement of this level in metal-carbon bonding. There will be a resultant movement of electrons into the $2\pi_{co}$ orbital. This motion of charge constitutes an oscillating electrical dipole associated with a vibration in the carbon-oxygen bond. The magnitude of the dipole oscillation caused by this 'orbital following' is considerable[59].

The magnitude of the oscillating electrical dipole associated with a given mode of vibration is important in determining the intensity of the observed infrared absorption due to that mode of vibration[60]. Thus, metal to ligand π-donation explains the high intensities observed in metal carbonyl infrared spectra.

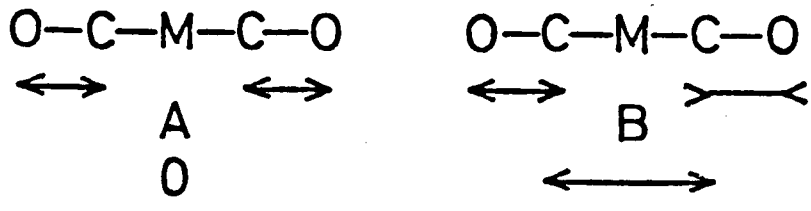
Since a good deal of the dipole change consequent on the vibration of a carbon-oxygen bond occurs in the metal-carbon bond, it is not surprising that strong dynamic coupling occurs between the individual carbonyl stretches in a multicarbonyl system. Of course, individual CO stretches interact with other motions within the molecule, particularly with metal-carbon stretches.

In formal treatments, an observed frequency is regarded as being a consequence of the total periodic change in molecular geometry. That is, the frequency of an observed metal carbonyl vibration depends on the interaction constants of that vibration with changes in every other internal co-ordinate of the molecule (where an internal co-ordinate is defined as a bond length, a bond angle, a through space interaction etc.) as well as on the force constant (and

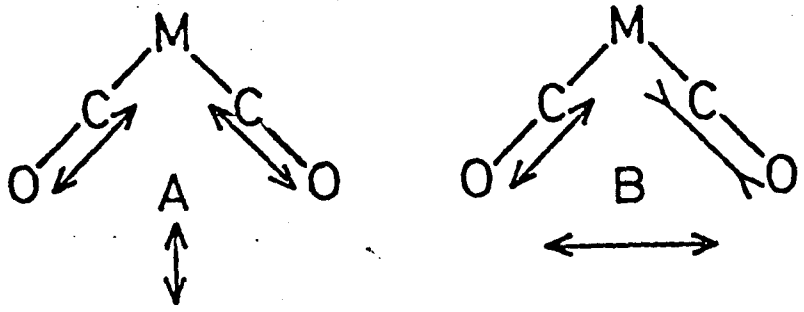
reduced mass) of the bond concerned. It transpires, from formal treatments, that interactions between internal co-ordinates depends, among other factors, on the similarity of the energies derived from the force constants and reduced masses associated with the individual internal co-ordinates. Fortunately, the carbonyl stretch is energetically isolated from other changes in internal co-ordinates in metal carbonyls. Thus, to neglect the effects of coupling interactions between carbonyl stretches and, say metal-carbon stretches, in determining frequencies is to make a serious but permissible approximation[61].

In less formal interpretations of metal carbonyl spectra, the effects of interactions of other motions, such as M-C stretches, on the observed 'carbonyl stretching frequencies' are commonly neglected.

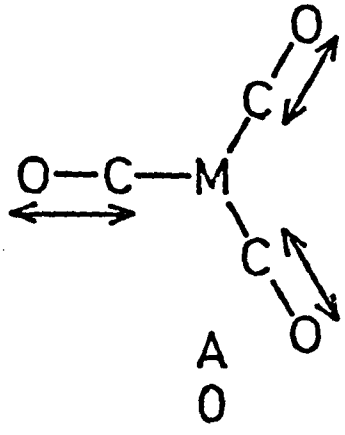
The normal modes of vibration for metal carbonyl moieties relevant to this work are illustrated in figure 7, together with schematic representations of the net molecular dipole oscillations.

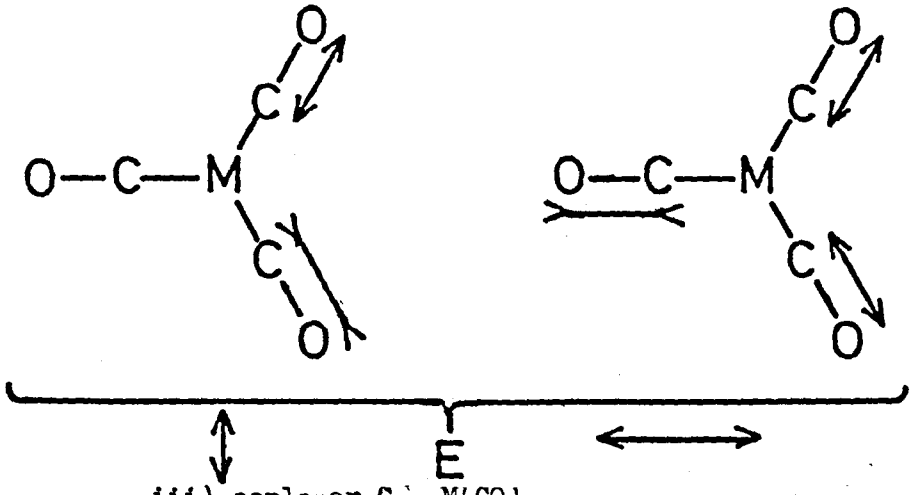


i) linear $M(CO)_2$



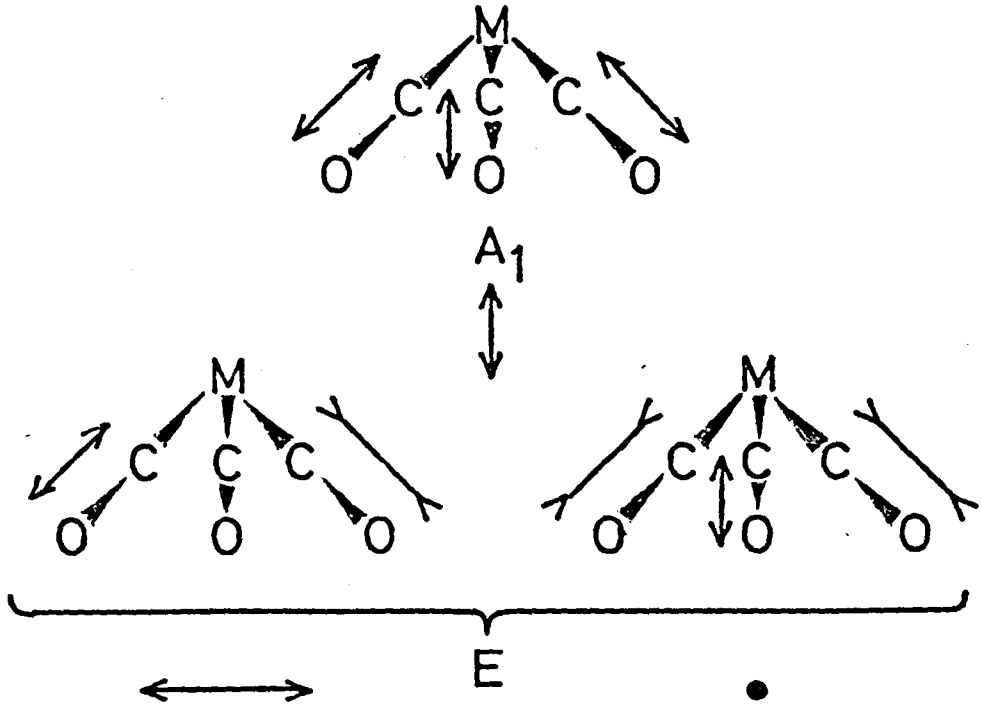
ii) non-linear $M(CO)_2$



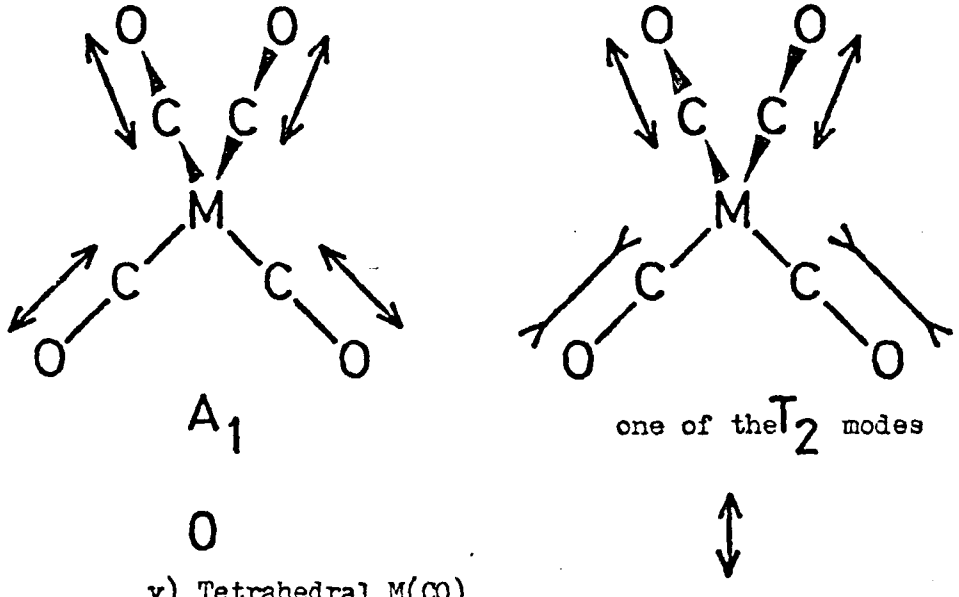


iii) coplanar G_{3v} $M(CO)_3$

following page 16 (i)



iv) non-coplanar C_{3v} $M(CO)_3$



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v) Tetrahedral $M(CO)_4$

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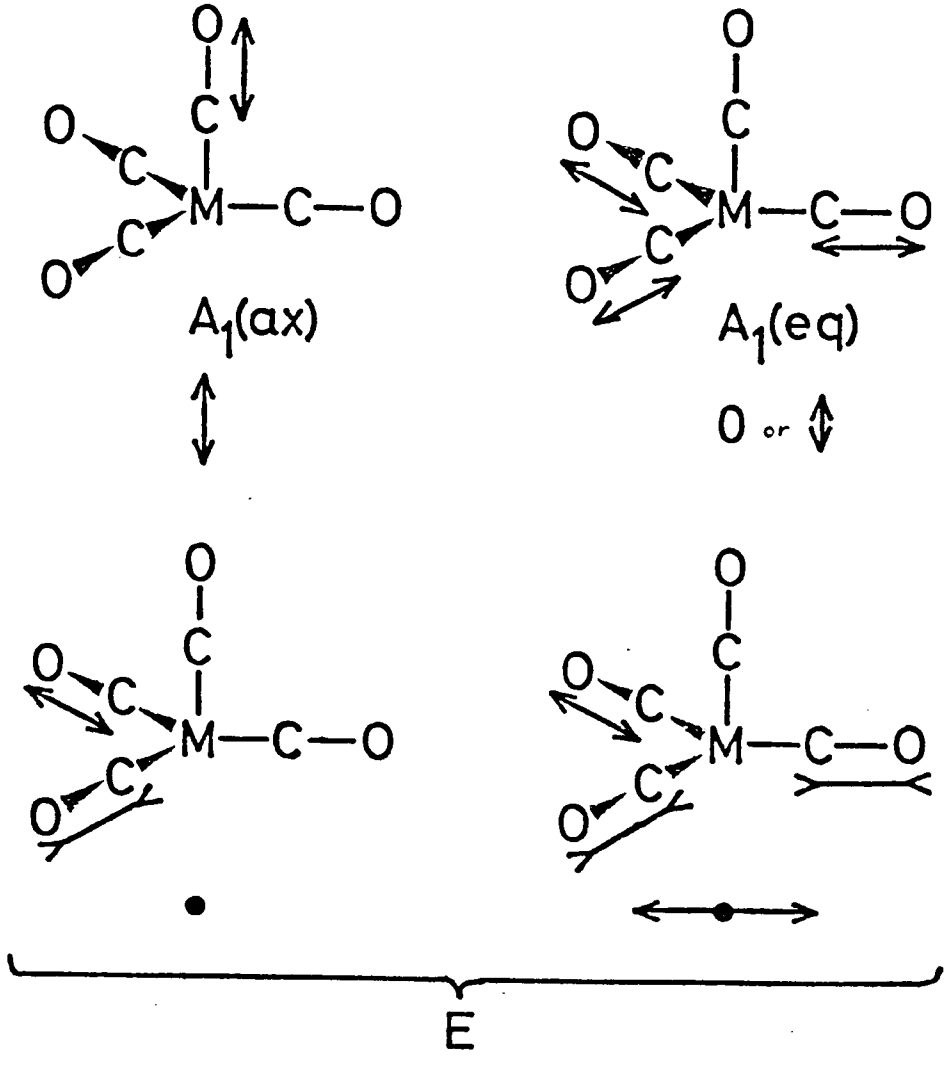


vi) $M(CO)_4$ in axially substituted trigonal bipyramidal $M(CO)_4L$.

Figure 7: Normal modes of vibration of some metal carbonyl species. Taken from reference 59. ● Represents an oscillating dipole perpendicular to the plane of the page.

It can be seen that the angle between the carbonyl groups is important in determining the magnitude of the overall oscillating dipole, and thus, also the intensity of the carbonyl region infrared absorptions. In the limiting case, the in-phase stretch of a number

of identical carbonyl groups arrayed under S_n or D_n symmetry will have zero intensity. (In real systems, the structure usually deviates from ideal symmetry either intrinsically, or under the influence of an external agent, such as the solvent or a partner in an ion pair. These bands, therefore, often appear, but are relatively weak.)

Comparison of the intensities of infrared bands has been used to distinguish between isomers differing in the disposition of their carbonyl groups[62]. More detailed studies have allowed more precise structural information to be derived[63].

The frequency of a given carbonyl stretching mode depends on the electron availability at the metal. A greater availability of electrons will encourage more π back donation. This will weaken the carbon-oxygen bond. In the isoelectronic, isostructural sequence, hexacarbonylvanadate(1-), hexacarbonylchromium and the hexacarbonylmanganese(I)cation, the major (T_{1g}) carbonyl bands appear at 1843 cm^{-1} (in THF)[64], 1984 cm^{-1} (in hydrocarbon)[65] and 2094 cm^{-1} (in THF)[64] respectively. The frequency, in this sequence, increases with increasing nuclear charge. The same trend is noted for the T_2 bands of tetracarbonylferrate(2-) (1786 cm^{-1} in water [66]), tetracarbonylcobaltate(1-) (1888 cm^{-1} in dimethyl formamide[67] and tetracarbonylnickel (2045 cm^{-1} in carbon tetrachloride[68]).

Two or more carbonyl groups stretching in phase compete for electron density. Whereas the same groups stretching out of phase do not. Therefore, it is to be expected that A_1 bands appear at higher frequency than do other bands arising from stretches of the

same carbonyl groups. This is found to be the case almost[69] without exception. Indeed, in polycarbonyls, A_1 bands due to several carbonyl groups tend to appear at higher frequency than those for a unique carbonyl group in the same molecule. There would be dangers in extrapolating this effect too far.

Replacing one carbonyl group on a multi carbonyl system with a poorer π-acceptor, such as a phosphine, will leave more electronic charge on the metal. This substitution would, therefore, be expected to lower the bond orders, and therefore, the stretching frequencies of the remaining carbonyl groups. This, again, is often found to be true. Since the σ-donor strength of a ligand is important in determining the electron density at the metal, the effects of the σ-donor strength of a ligand, as well as its π-acidity must be considered: it is often impossible to extricate the two effects.

A rough order of π-accepting ability can be derived from the effects of the ligands on the dominant carbonyl stretching frequency of the (ligand) nickel tricarbonyl series described in table 1.

$Ni(CO)_3L$	$\nu(E)$ (cm^{-1})	Reference
$L = PF_3$	2049	70
PCl_3	2044	71
$P(OMe)_3$	2015, 2006*	72
PMe_3	1994	72
CO	(νT_2-)2045	68

Table 1: The major carbonyl stretching frequency for a series of tricarbonyl (ligand) nickel species.

*Splitting due to the presence of two conformers, dictated by the ligand.

It can be seen that in the derivatives of PX_3, the classical electronegativity of the group, X, is important in determining the π-acidity of the phosphorus base.

Phosphorus, arsenic, antimony and even bismuth bases all act as π-acids towards metals of all three transitions. Nitrogen bases, however, are very much poorer π-acceptors as can be seen from table 2. This is attributed to the lack of an energetically accessible d orbital on nitrogen:

$Cr(CO)_5L$	$\nu(E)(cm^{-1})$
$L = NH_3$	1921
PH_3	1953
AsH_3	1951
SbH_3	1956

Table 2: The major carbonyl stretching frequency for a series of pentacarbonyl (ligand) chromium species[73].

Many other moieties act as π-acceptors towards metals. The most important of these are unsaturated organic groups, in which the antibonding π system may accept electron density. Figure 8 illustrates the bonding interactions between a metal and ethylene.

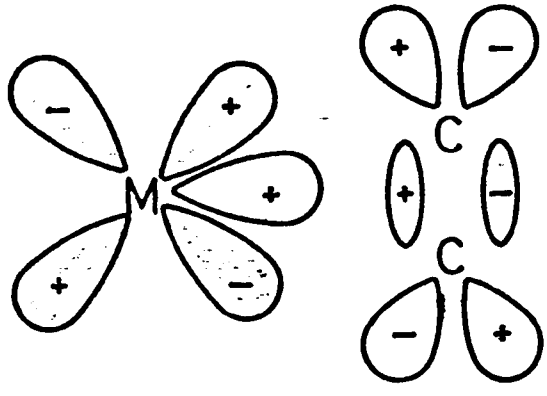


Figure 8: The bonding interactions between an olefin 1π (bonding) orbital and a lobe of an empty metal hybrid, and

between a metal d orbital and the empty 2π (antibonding) olefin orbital.

SECTION THREE: COBALT CARBONYL

a) Historical

In his original paper on tetracarbonylnickel[12], Ludwig Mond announced failure to produce carbonyls of cobalt or iron by passing carbon monoxide over the hot metals.

In 1908, Mond prepared octacarbonyldicobalt by the high pressure hydrogen reduction of cobaltous oxide in the presence of carbon monoxide[74]. The orange crystals were found to be unstable in air, reacting to give basic cobaltous carbonate. Cobalt carbonyl occasionally inflames in air. Mond also recognised that octacarbonyldicobalt was thermally unstable, losing carbon monoxide to give black crystals of empirical formula, $Co(CO)_3$[13].

Apart from the discovery of nitrosyltricarbonylcobalt(I) by Mond's son, Robert in 1922[75], very little work on cobalt carbonyls was reported between their discovery and the outbreak of the second world war.

Interest appears to have been confined to methods of improving the high pressure reductive synthesis of the metal carbonyl[e.g.76]. It may, or may not, have been suspected that cobalt carbonyl was involved in the recently announced Fischer-Tropsch reaction[30] but at least some of the interest in the species was directed at ways of purifying the metal[76a].

An inefficient ambient temperature, atmospheric pressure synthesis of cobalt carbonyl from the corresponding sulphide or

cyanide[77] was reported in 1934 and improved upon in 1940[78].

When Hieber reviewed the metal carbonyls in 1942[79] the discussion on dicobalt octacarbonyl was limited to topics such as stability and high pressure formation reactions.

Although Hieber had begun the investigations of the chemistry of cobalt carbonyls in 1937[80], wide interest was not aroused in the chemistry of these compounds until it was shown in 1948, that they were the true hydroformylation catalysts[81].

b) Descriptive

The solid state structure of octacarbonyldicobalt has been reported[82]. This shows that two of the carbonyl groups bridge the two cobalt centres (figure 9).

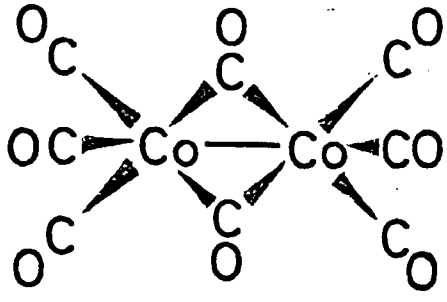


Figure 9: Schematic representation of the solid state structure of $Co_2(CO)_8$ based on ref. 82.

The precise structure(s) of octacarbonyldicobalt in solution was the topic of some debate for several years. The earliest spectral analyses of octacarbonyldicobalt[83] showed the presence of a band at 1858 cm^{-1}. It was proposed that this band was due to a 'ketonic' bridging carbonyl stretch[84]. Disagreement occurred over

the precise structure of this species[84,85]. Indeed caution was expressed over the assignment of the band to a bridging carbonyl species[85].

With the advent of improved spectrometer optics, re-investigations of the spectrum of octacarbonyldicobalt were commenced[86]. In 1963, Bor[87] and Noack[88] independently explained the infrared spectrum of octacarbonyldicobalt in terms of a mixture of a bridged species closely resembling the solid state structure and a non-bridged isomer. Bor[89] disagreed with Noack's proposal for the precise structure of the non-bridged species. The problem was finally resolved as late as 1974 when Bor and Noack showed that the second isomer has a structure similar to that illustrated in figure 10a[90].

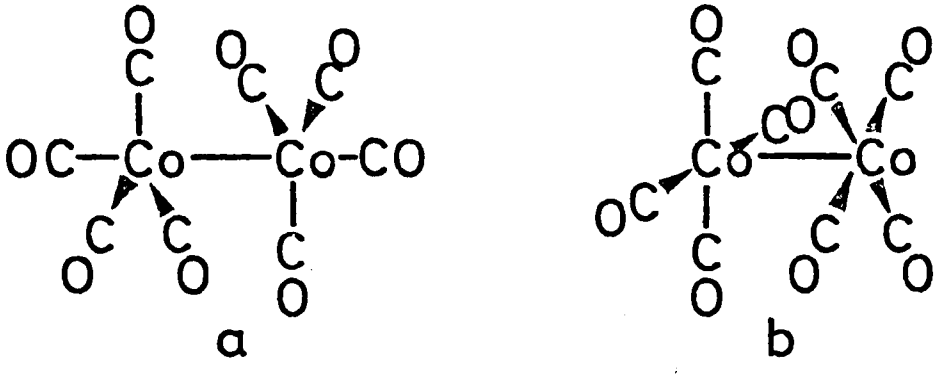


Figure 10: The unbridged isomers of $Co_2(CO)_8$ after ref. 90.

In the same paper, Noack and Bor tentatively suggested the presence of another unbridged isomer in solutions of octacarbonyldicobalt. The proposed structure consists of two

parallel, staggered square-planar $Co(CO)_4$ groups linked by a perpendicular Co-Co bond (figure 10b). In 1976, Bor and Noack were able to show that octacarbonyldicobalt in fact exists in three significant isomeric forms. A temperature dependent equilibrium exists between the three species, favouring the lately discovered isomer at high temperature, and the bridged form at low temperature[91].

Several other neutral cobalt carbonyls are known to exist. Carbonylcobalt, CoCO, dicarbonylcobalt, $Co(CO)_2$, tricarbonylcobalt, $Co(CO)_3$, and tetracarbonylcobalt, $Co(CO)_4$, have been formed by metal atom synthesis techniques in inert gas matrices[92]. Tetracarbonylcobalt shows significant trigonal distortion from tetrahedral symmetry.

The environment in which these species have been formed can be said to be remote from chemical reality. However, the infrared spectrum of tetracarbonylcobalt has been recognised in solution at temperatures over 120°C[91]. The possibility of spectroscopically insignificant, but chemically significant occurrence of tetracarbonylcobalt in cobalt carbonyl containing reaction mixtures cannot be overlooked. (The dissociation energy of the $(OC)_4Co\text{-}Co(CO)_4$ bond has been shown to be only 61 ± 8 kJ mol^{-1}[93]. Since tetracarbonylcobalt was recognised under 120 atmospheres of carbon monoxide, the possibility of the existence of tricarbonylcobalt in reaction mixtures at much lower carbon monoxide pressure must be considered. By analogy with the dissociation of CO from octacarbonyldicobalt (vide infra), the equilibrium concentration of tricarbonylcobalt in any solution of octacarbonyldicobalt would be expected to be vanishingly small, but, again by analogy with the dissociation of CO from octacarbonyldicobalt, the rate of its

formation from tetracarbonylcobalt would be expected to be extremely high.

Hexacarbonyldicobalt and heptacarbonyldicobalt have not been recognised as independent species, but have been postulated as intermediates in reactions of octacarbonyldicobalt[94,95], in convincing kinetics studies. The concentration of heptacarbonyldicobalt has been estimated[94] to be about 0.1% of that of octacarbonyldicobalt at 25 °C in heptane under one atmosphere of CO.

At extremely high (393 atmospheres) carbon monoxide pressure, octacarbonyldicobalt absorbs one molecule of the gas. It has been proposed, by Wender, Metlin and Sternberg[96] that the incoming carbonyl group may cause valence disproportionation of the carbonyl to give pentacarbonylcobalt(I) tetracarbonylcobaltate(1-). Under similar conditions, Whyman[97] failed to detect the presence of tetracarbonylcobaltate. Whyman proposes the presence of (μ-carbonyl)octacarbonyldicobalt: In order for this species to obey the eighteen electron rule, it must contravene Cotton's generalisation[98] that carbonyl bridges occur only in the company of direct metal-metal bonds. It appears unlikely that nonacarbonyldicobalt, whatever its form is significant in determining the course of syntheses starting from octacarbonyldicobalt. The presence of a nonacarbonyldicobalt species in the hydroformylation reaction has been proposed[99], but the species appears not to be involved in the hydroformylation reaction itself[99,100].

There is evidence for the existence of octacarbonyltricobalt, but the species has not been characterised spectroscopically or otherwise.

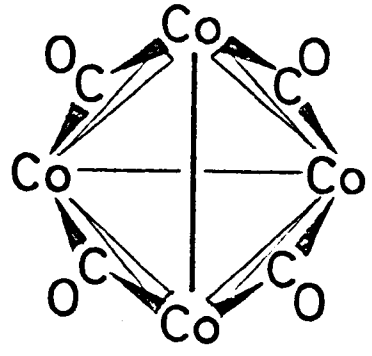
Gankin and coworkers[101] believe that the intermediate arises by valence symproportionation of the salt cobalt (II) bis-(tetracarbonylcobaltate(1-)). (The ligands in the divalent cobalt species, if any, are not mentioned.) Chini[102] has assumed that octacarbonyltricobalt may be formed by the loss of ethanol from the salt, $[Co(C_2H_5OH)_x][Co(CO)_4]_2$ or by reaction of dodecacarbonyltetracobalt with an alkali metal, as shown in equation (4).

$$Na + Co_4(CO)_{12} \longrightarrow NaCo(CO)_4 + Co_3(CO)_8 \quad \text{---- (4)}$$

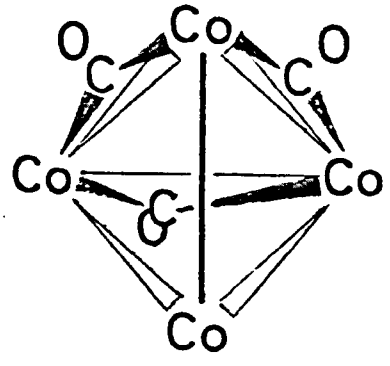
Dodecacarbonyltetracobalt is formed by the thermal decomposition of octacarbonyldicobalt. 'Cobalt tricarbonyl' has, therefore, been known for as long as the latter species[13], although it was not recognised to exist as the tetramer until a molecular weight determination was accomplished by Hieber in 1932[103].

The determination of the solid state structure of dodecarbonyl tetracobalt was complicated by the fact that the crystal structure is disordered. A structure was proposed by Corradini in 1959[104]. This structure was confirmed by Wei in 1969[105]. The structure is described by Wei as follows: 'Each molecule consists of an apical $M(CO)_3$ group co-ordinated by three metal-metal bonds to a basal $M_3(CO)_9$ fragment containing three chemically identical $M(CO)_2$ groups linked to each other by metal-metal bonds and bridging carbonyl groups'.

The solution infrared spectrum of dodecacarbonyltetracobalt[86,106] was found to deviate slightly from that predicted for Corradini's structure. An alternative structure was suggested by Smith[107]. The positions of the bridging carbonyl groups in these structures are indicated in figure 11.



a



b

Figure 11 : Structures for $Co_4(CO)_{12}$

a) Suggested by Smith [107]

b) The solid state structure [104,105]

following p. 26

Cotton pointed out that the existence of both of these structures in solution could be accomodated by assuming that dodecacarbonyltetracobalt is stereochemically non-rigid[108]. Cotton proposed a mechanism for the interconversion of the two forms via the intermediacy of a transient "all-terminal" isomer. The ^{59}Co nmr spectrum of dodecacarbonyltetracobalt has been shown to comprise two signals in the ratio 3:1[109,110]. This would imply that Corradini's structure, if not the sole species present, is at least the dominant isomer. The low temperature ^{13}C n.m.r. spectrum of the dodecacarbonyl however, shows three signals of approximately equal intensities, consistent with the presence of two types of terminal, and one bridging environment[111]. At higher temperatures, the carbonyl groups appear to become scrambled, indicating that the molecule is, indeed, stereochemically non-rigid (Cobalt-59 imposes temperature dependent quadrupole broadening on the ^{13}C n.m.r. spectra of cobalt carbonyls[112], and so it was impossible for Lewis, Johnson and coworkers[111] to observe a time-averaged signal from the carbon nuclei). The question as to which species is dominant in solution at room temperature remains open.

The only known reasonably stable high nuclearity metal carbonyl cluster compound containing solely cobalt and carbon monoxide is hexadecacarbonylhexacobalt[102]. The infrared spectrum of this species shows it to be isostructural with hexadecacarbonylhexarhodium. The solid state structure of hexadecacarbonylhexarhodium has been shown[113] to consist of six $Rh(CO)_2$ groups situated at the apices of an octahedron. Each Rhodium centre is linked to the four neighbouring metal atoms by a metal-metal bond. In addition, triply bridging carbonyl groups are situated above alternate faces of the octahedron.

Hexadecacarbonylhexacobalt decomposes in the presence of one atmosphere of carbon monoxide to give dodecacarbonyltetracobalt[114]. The infrared spectrum of the hexanuclear cobalt species is readily distinguishable from that of dodecacarbonyltetracobalt, since the triply bridging carbonyl absorption of the former occurs at substantially lower frequency than the doubly bridging carbonyl band of the latter.

No cationic homoleptic cobalt carbonyls have been identified. The Pentacarbonylcobalt(I) cation has been tentatively proposed by Metlin, Wender and Sternberg[96] (vide supra).

Several anionic cobalt carbonyls are known. By far the most important of these is the tetracarbonylcobaltate(1-) anion. This species is isoelectronic and isostructural with tetracarbonylnickel. In fairly polar media, such as (wet) THF, tetracarbonylcobaltate exhibits only one infrared band in the carbonyl stretching region (at 1886 cm^{-1}). This is the triply degenerate out of phase stretch of a perfect tetrahedron[115].

In non-polar solvents, sodium tetracarbonylcobaltate(1-) may form a number of types of ion grouping. Formation of the contact ion pair between Na^+ and tetracarbonylcobaltate(1-) causes significant trigonal distortion of the anion. The totally symmetric stretch becomes visible at 2005 cm^{-1}, and the T_2 band is split into an A_1 band (1855 cm^{-1}) and an E band (1898 cm^{-1}). Other geometries result from the formation of solvent separated in pairs, triple ions and so on[116].

Tricarbonylcobaltate(1-) has been observed only following gas

phase electron bombardment of octacarbonyldicobalt [117]. The possibility of the transient existence of this species following valence disproportionation of dodecacarbonyltetracobalt cannot, however, be overlooked.

Fieldhouse, Freeland, Mann and O'Brien[118] have reported that decacarbonyltricobaltate monoanion is formed in the alkali metal reduction of octacarbonyldicobalt. The infrared spectrum implies the presence of terminal, bridging and triply bridging carbonyl groups, but the precise structure has not been determined. The unique triply bridging carbonyl group acts as a Lewis acid towards trimethylamine iodoborane and trimethylchlorosilane[119].

When dodecacarbonyltetracobalt is reduced by alkali metals, tetradecacarbonylhexacobaltate tetra-anion and pentadecacarbonylhexacobaltate dianion are formed[120]. These anions readily accept carbon monoxide to give tetracarbonylcobaltate[121,102]. When bis-(π-cyclopentadienyl)Cobalt(II) is employed as the reducing agent, an intermediate complex salt containing the undeca- or dodecacarbonyltetracobaltate mono-anion is formed.

SECTION FOUR : THE METAL-CARBON BOND

Reference has been made to the bonding interactions between a metal and an olefin (p20).

In 1949, Chatt showed unequivocally that ethylene acts as a co-ordinating ligand towards platinum. The mode of co-ordination was described as 'side-on' with the olefin donating electron density from its π-bonding orbitals to the transition metal[122]. Chatt's conclusions had tremendous implications for the future of transition metal organic chemistry.

Two years later, the discovery of a ferrocene was announced by Kealy and Pauson[123] and, independently by Miller, Tebboth and Tremaine[124].

The now accepted sandwich structure of ferrocene was suggested by Wilkinson, Rosenblum, Whiting and Woodward[125] in 1952. Very shortly afterwards, a number of suggestions for the electronic structure were made[126] which were, consciously or otherwise, based on Chatt's model for olefin-platinum bonding.[122a]

Modern transition metal organic chemistry was thus born in the early 1950's. Many organo-transition metal compounds were, however, known prior to this. It was perhaps the enigmatic, even contradictory nature of the salt, potassium trichloro(ethylene)platinate discovered by W.C. Zeise, professor of chemistry at Copenhagen, in 1827[127] that accounted for the recurring interest in olefin-platinum compounds.

Controversy existed over the nature of the anion for several years after its discovery[128,129].

In 1861, Griess and Martius thermolysed Zeise's salt and observed the evolution of ethylene[130]. Other investigations of platinum-ethylene complexes were carried out periodically over the next ninety years[131], culminating in the work of Chatt.

Prior to the discovery of ferrocene, very few complexes of unsaturated organic groups with transition metals, apart from platinum, were known: A few palladium-olefin compounds had been prepared[132], as had dichloro(ethylene)iridium(II)[133]. (η^4-butadiene)tricarbonyliron had been reported[134]. Polyphenylchromium

species had been studied[135], but these were not recognised to be dibenzenechromium derivatives until 1956[136].

Compounds containing carbon bound to a transition metal solely by a σ bond were even more elusive than compounds now known to contain π-bound organic ligands. A group of stable methyl platinum compounds was discovered by Pope and Peachy in 1907[137]. Gibson[138] had announced a series of gold (III) alkyls in the 1930's. Work was being carried out on compounds containing alkyl-titanium bonds, including $R_nTiX_{(4-n)}$ (R=alkyl, X=halide)[139], a grouping later to become important in Ziegler and Ziegler-Natta polymerisations[140].

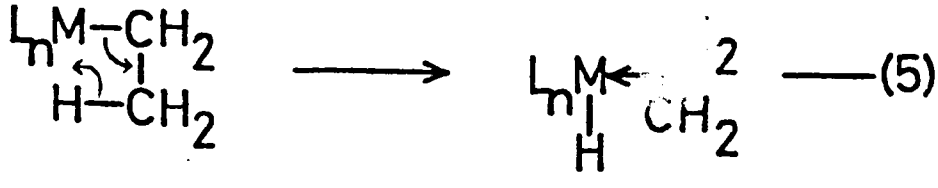
Excepting platinum compounds, group VIII alkyls and aryls were virtually unknown in 1955[141]. Cobalt was fairly atypical in that a few σ-naphthyl cobalt compounds had been discovered before ferrocene[142].

Since the dearth of transition metal alkyls and aryls could not be ascribed to failure to attempt the synthesis of such compounds[141], the conclusion that metal carbon σ bonds are inherently weak[143] was not an unnatural one to draw.

With the upsurge of interest in transition metal organic chemistry in the 1950's, the number of known transition metal alkyls proliferated. Success in synthesising molecules containing metal-carbon σ bonds was particularly high in cases where the metal group was attached to some other strongly co-ordinating ligands. Metal carbonyls were prominent in this group. Methylpentacarbonylmanganese(I)[25,26], methylpentacarbonylrhenium(I)[144] and methyltetracarbonylcobalt(I)[145] were all identified in the late 1950's.

Chatt and Shaw[146] were successful in synthesising a huge number of alkyl derivatives of the nickel group metals where trialkylphosphine ligands were also present on the metal. This led them to conclude that the presence of π-acceptor ligands 'conditioned' the metal for metal-carbon σ bonding. They proposed that in the absence of π-accepting ligands, the metal carbon bond cleaved via an initial step which involved promotion of an electron from the highest occupied to the lowest unoccupied molecular orbital. (The lowest unoccupied orbital being a metal-carbon antibonding interaction). Since metal-carbon π-bonding affects the energies of the metal d orbitals, it was argued that the ene- - required for the initial electron promotion, and therefore, the activation energy for M-C bond cleavage, could be raised by the influence of supporting π-acid ligands.

Evidence began to accumulate in the 1960's that metal-carbon bond homolysis was not the only, indeed, not the major, way in which organometallic compounds thermally decompose: Ethyl metal derivatives were found to evolve ethylene and leave the corresponding metal hydride. Higher metal alkyls behaved analogously. This has been described as the electrocyclic β-elimination proce 5)[147].



Reductive elimination (6) has been postulated in explanation of the formation of methane from methyl metal hydrides[148] and dialkyl

from metal dialkyls[149,150].

$$L_nMR_2 \longrightarrow L_nM + R_2 \quad \text{——— (6)}$$

where R is usually an alkyl or aryl group or hydrogen.

These, and several other concerted reactions involving metal alkyls led Wilkinson[151] to surmise that the role of the supporting ligands is to block the possibility of these concerted decompositions. This they do by obstructing the co-ordination sites required by the decomposition pathways, and by satisfying the metal's electronic requirement. (For non-transition metals, for which only 18-electron compounds of a preferred geometry are commonly found, decomplexation of a supporting ligand is often found to be a prerequisite for decomposition by the β-elimination route).

By considering crystallographic bond length and spectroscopic force constant data, Braterman and Cross concluded that the carbon transition metal bond is in no qualitative way different from carbon-main group metal bonds[152]. The same workers have shown that several of the very compounds used by Chatt and Shaw in formulating their theory, in fact decompose by concerted pathways[153].

Transition metal alkyls may decompose by homolytic scission of the metal-carbon bond[154], but (perhaps due to the shift of focus towards concerted mechanisms) no recent studies of the effects of supporting ligands on determining the likelihood of homolysis have been carried out. Bond strength estimations may be helpful, but could not, in themselves be used to predict whether or not homolytic or concerted decomposition of a particular compound is likely to occur.

Metal alkyls commonly (not necessarily) contain the metal in a low oxidation state. One stabilising effect of π-accepting ligands that is presumably not in doubt is that, by decentralising electron density, they render the system less susceptible to electrophilic attack. That is, π-acceptance increases the oxidative stability of the metal compound.

SECTION FIVE : ALKYLTETRACARBONYLCOBALT(I) SPECIES IN SYNTHESIS

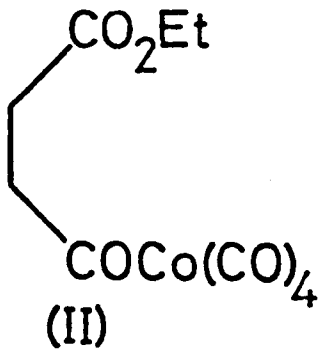
The formation of a range of organic products via what are now recognised to be organocobalt intermediates in the numerous metal/carbon monoxide catalytic processes has been described earlier. The use of organocobalt carbonyls in synthesis grew out of these catalytic reactions, particularly, the OXO process.

Heck proposed the intermediacy of cobalt carbonyl alkyls in the hydroformylation process[39].

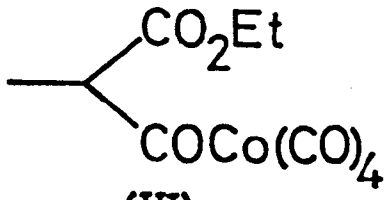
Hydridotetracarbonylcobalt(I), formed by the reaction of octacarbonyldicobalt (or heptacarbonyldicobalt) with hydrogen[e.g.100] may formally add across the double bond of the olefin involved to give this alkyl cobalt intermediate (7):

$$RCH_2{=}CH_2 + HCo(CO)_4 \longrightarrow \underset{\displaystyle CH_3}{\overset{|}{R}}CHCo(CO)_4 \quad (7)$$
$$+ RCH_2CH_2Co(CO)_4$$

Takegami has shown[155] that the addition of hydridotetracarbonylcobalt(I) to ethyl acrylate gives the succinic acid derivative, (II) as the major product at higher temperature, but mainly the methylmalonic acid derivative, (III) at lower temperatures.



(II)



(III)

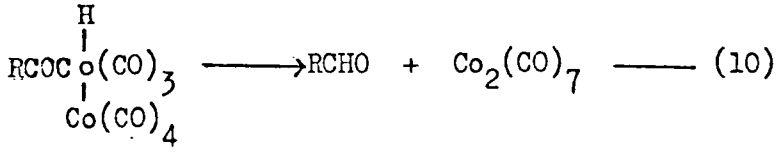
This suggested to Takegami that hydridotetracarbonylcobalt(I) acts as a pseudo hydrohalic acid towards olefins: The preferred direction of attack on the olefin linkage is that which gives rise to intermediate (III). Intermediate (II) is formed from (III) at higher temperatures by an isomerisation reaction which will be more fully discussed in Chapters three and four.

Pent-1-ene reacts with hydridotetracarbonylcobalt(I) to give mainly n-pentyltetracarbonylcobalt(I). The relative amounts of this product and 1-methylbutyl cobalt tetracarbonyl formed appear not to depend on temperature. Whether this indicates that isomerisation of the branched to the straight chain isomer is extremely ready in this case, or that anti-Markovnikov addition occurs remains to be determined.

Heck has suggested[156] that alkyl cobalt tetracarbonyls are decomposed by hydridotetracarbonylcobalt(I) by the following mechanism:

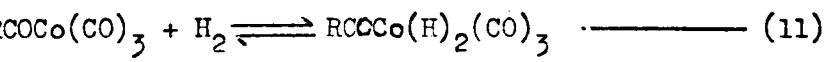
$$RCo(CO)_4 \rightleftharpoons RCOCo(CO)_3 \qquad (8)$$

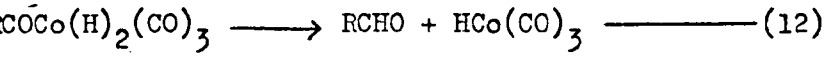
$$RCOCo(CO)_3 + HCo(CO)_4 \rightleftharpoons RCO\underset{\displaystyle Co(CO)_4}{\overset{\displaystyle H}{Co}}(CO)_3 \qquad (9)$$



Process (9) could be described as oxidative addition of the carbonyl hydride to the co-ordinately unsaturated acyl tricarbonyl cobalt species. Process (10) represents reductive elimination of the aldehyde from the divalent cobalt centre formed in (9).

Markó[157] has suggested that acyl cobalt tricarbonyl may itself suffer oxidative addition by dihydrogen (11);





The trivalent cobalt intermediate decomposes by reductive elimination to the aldehyde and hydridotricarbonylcobalt(I).

Heptacarbonyldicobalt and hydridotricarbonylcobalt(I) would both be expected to pick up carbon monoxide under the conditions of the hydroformylation reaction.

It would be difficult to distinguish between Markó's mechanism for the formation of aldehydes and Heck's since hydridotetracarbonylcobalt(I) is sure to form in solutions containing cobalt carbonyls under high pressures of hydrogen. It is not impossible of course that both mechanisms operate in the hydroformylation process.

In 1964, Beck and Nitzschmann recognised acetone among the volatiles ensuing from a synthesis of methyltetracarbonylcobalt(I).[158] Diethyl ketone was similarly generated from ethyl iodide and carbon monoxide in the presence of sodium tetracarbonylcobaltate(1-).

Heck explained this observation in terms of a reaction scheme[156,159] not dissimilar to that which he had proposed for the decomposition of alkyl cobalt tetracarbonyl by hydridotetracarbonylcobalt(I). In this case, acyl cobalt tricarbonyl suffers oxidative addition of alkyltetracarbonylcobalt(I) (13). Reductive elimination from the divalent cobalt centre thus formed gives the ketone and heptacarbonyldicobalt (14).

$$RCOCo(CO)_3 + RCo(CO)_4 \longrightarrow \begin{matrix} COR \\ | \\ RCo(CO)_3 \\ | \\ Co(CO)_4 \end{matrix} \quad \text{——— (13)}$$

$$\begin{matrix} R \\ | \\ RCo(CO)_3 \\ | \\ Co(CO)_4 \end{matrix} \longrightarrow R_2CO + Co_2(CO)_7 \quad \text{——— (14)}$$

In the absence of carbon monoxide, heptacarbonyldicobalt undergoes a ligand disproportionation which results in the formation of octacarbonyldicobalt and dodecacarbonyltetracobalt.

Primary and secondary amines, alcohols[160] and water[161] have been shown to bring about the degradation of alkyl- and acyl- cobalt tetracarbonyls. Amides, esters and carboxylic acids respectively are formed.

Thermal decomposition, reductive cleavage (by hydrogen or hydrides) and decomposition by bases are the major methods of obtaining organic products from organocobalt carbonyl intermediates.

Oxidative cleavage of the acyl-cobalt bond can be brought about. This method has been employed to derive acyl halides (15)[162]

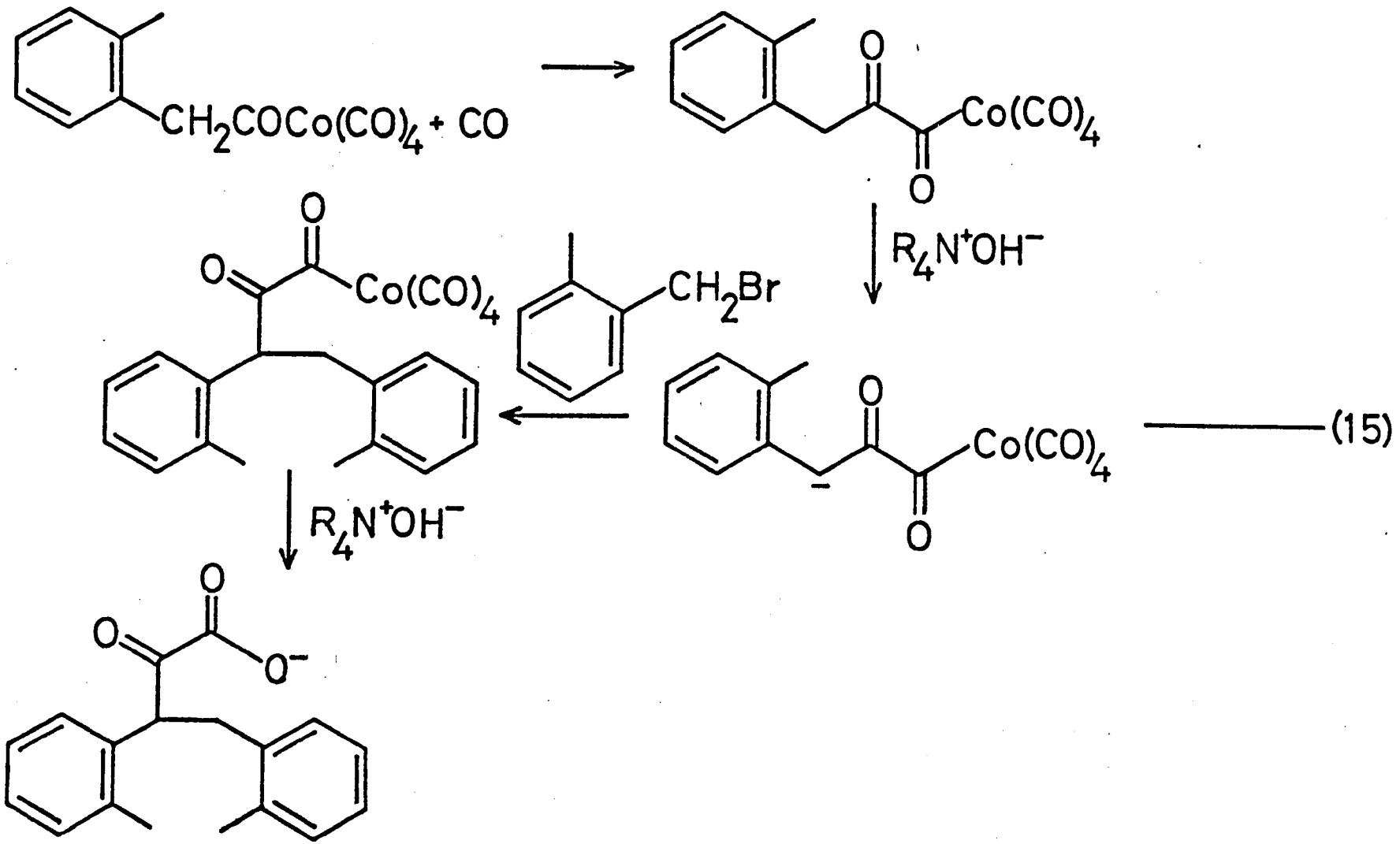
$$2\ RCOCo(CO)_4 + 3I_2 \longrightarrow 2\ RCOI + 8\ CO + 2\ CoI_2 \quad \text{——— (15)}$$

The synthetic importance of alkyltetracarbonylcobalt(I) is (or is likely to be) that several internal re-arrangements, dictated by the nature of the alkyl group, may occur prior to decomposition. Also, several species may be 'inserted' into the metal-carbon σ-bond of the acyl and alkyl derivatives.

The most important case in the latter groups is, of course, carbon monoxide insertion (or 1,2-alkyl migration) in alkyl cobalt tetracarbonyl. This leads to the formation of the acyl derivatives required in the production of all of the carbonylated derivatives obtained by this method.

Insertion of carbon monoxide into an acyl-cobalt bond does not appear to be general. To date the only reported 'double carbonyl insertion' reaction accounts for the formation of 2-oxo-3, 4-bis-(o - tolyl)-butanoic acid in respectable yield, from o-tolylacetyltetracarbonylcobalt(I).

The reaction may be carried out under one atmosphere of CO(15)[163]



(15)

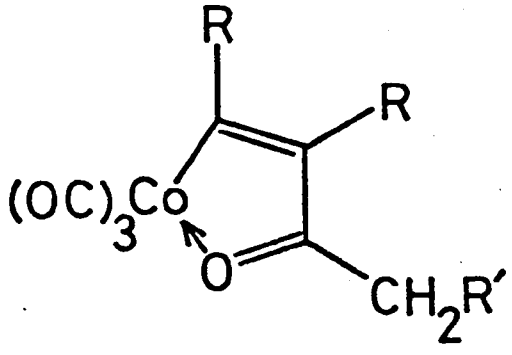
following page 38

(Tetra-alkyl ammonium hydroxide also serves to form tetracarbonylcobaltate(1-) from octacarbonyldicobalt, and α-bromo-o-xylene is the starting material from which o-toluylacetyltetracarbonylcobalt(I) had been formed).

The insertion of olefins into the cobalt-acyl bond has been shown to be of synthetic utility. For example, 2-propionyltetracarbonylcobalt(I) adds across the ethylene double bond to give 3-oxo-pentyltetracarbonylcobalt(I) which may then be reduced to diethyl ketone[164]. (The possible formation of 3-oxo-2-methylbutylcobalt tetracarbonyl is immaterial in this case.)

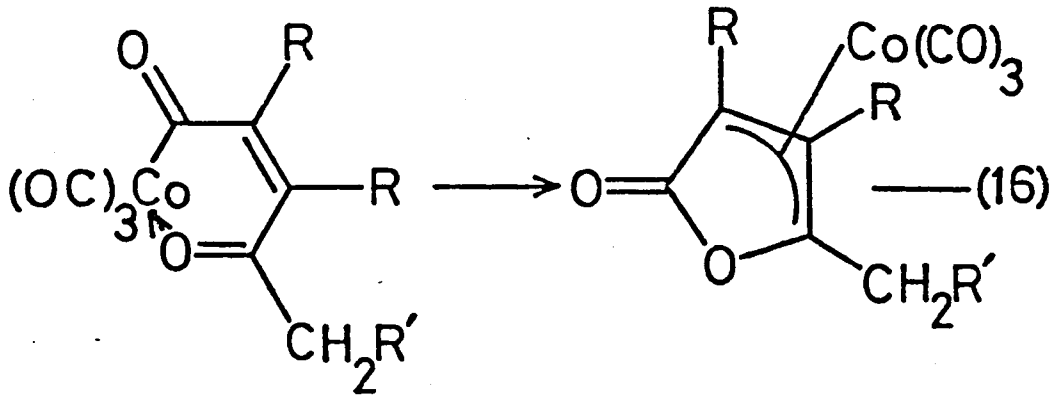
Where a double bond is suitably positioned within the acyl group, intramolecular olefin insertion may be suffered by acyl tetracarbonylcobalt(I): 5-hexenoyltetracarbonylcobalt(I) decomposes to give cyclohex-2-en-1-one, 2-methylcyclopent-2-en-1-one and 2-methylcyclopentanone[164].

Insertion of acetylenes into cobalt acyl bonds is found to give rise to cyclic intermediates of the type (IV)[165].



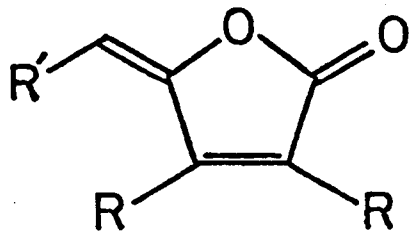
(IV)

Carbon monoxide rapidly inserts into the cobalt vinyl bond of (IV) to give (V). Insertion of the ketone double bond into the cobalt acyl bond in (V) gives the π-allyl derivative (VI) (16).



(V) (VI)

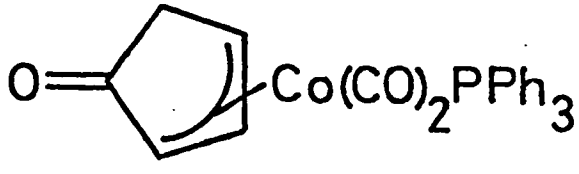
The elements of hydridotricarbonylcobalt(I) are abstracted from (VI) by hindered amines. The dienolactone, (VII) results.



(VII)

In a similar process, (IX) has been formed following the intramolecular insertion of a conjugated diene into the cobalt acyl bond in (VIII)[166].

$CH_2{:}CH{\cdot}CH{:}CHCOCo(CO)_3PPh_3$ —(VIII)

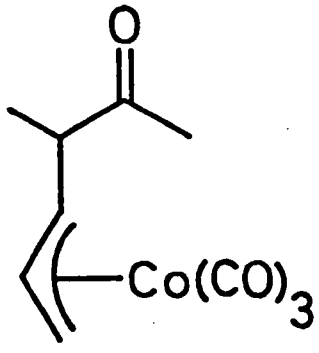


(IX)

Elimination of the elements of

hydridotricarbonyl(triphenylphosphine)cobalt(I) gives cyclopentadienone.

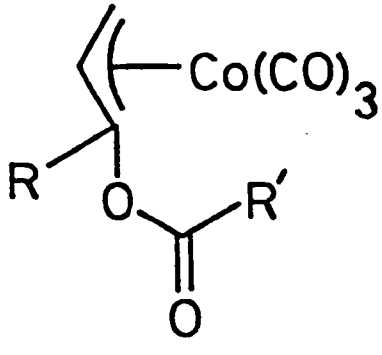
The intermolecular reaction of acyl tetracarbonyl cobalt(I) with butadiene gives (X)[167].



(X)

This method has been employed in the production of elusive acyl dienes. For example, 1,3-cyclohexadiene reacts with acetyltetracarbonylcobalt(I) and a base to give 1-acetyl-1, 3-cyclohexadiene[168].

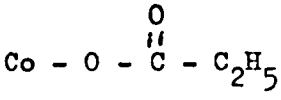
The carbon oxygen double bond of a conjugated enone may be inserted into an acyl carbon-cobalt bond (cf (16) above) intermolecularly to give a derivative of the type, (XI)[169].



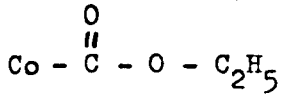
(XI)

The possibility of the insertion of small inorganic molecules into the cobalt-alkyl bond has received less attention than has the same process involving other metals.

Vol'pin and co-workers[170] have succeeded in adding ethylcarbonyl-bis-(triphenylphosphine)-cobalt(I) across a carbon oxygen bond of carbon dioxide. The addition can take place in either direction: Intermediates (XII) and (XIII) are formed.



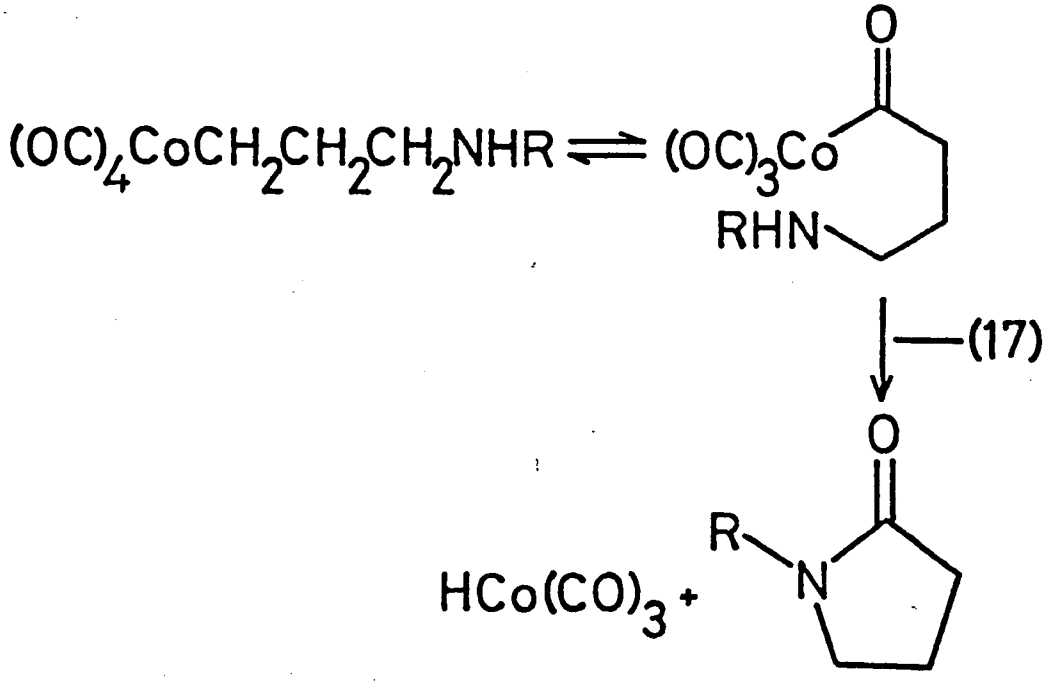
(XII)



(XIII)

Methyl iodide reacts with (XII) and (XIII) to give methyl propionate and ethyl acetate respectively.

Alcoholysis and aminolysis of acyl cobalt carbonyls may, in some cases, be brought about intramolecularly. N-alkyl allylamine reacts under hydroformylation conditions to produce N-alkyl pyrrolidone[171]. Falbe has proposed[172] the intermediary of an alkyl cobalt derivative which cyclises according to (17):



Falbe has extended this process to the production of other lactams, lactones (from allyl alcohol derivatives) and cyclic imides (from acrylamide derivatives). Only five- and six-membered ring products have been formed.

Clearly, the decomposition of acyl cobalt tetracarbonyls affords routes to numerous carbonylated products.

CHAPTER TWO

THE FORMATION OF TETRACARBONYLCOBALTATE(1-)

CHAPTER TWO : THE FORMATION OF TETRACARBONYLCOBALTATE(1-)

SECTION ONE : INTRODUCTION

Salts of tetracarbonylcobaltate(1-) may be produced from neutral cobalt carbonyls either by direct reduction or by valence disproportionation.

Direct reduction may be brought about electrochemically[133], or by using strong reducing agents such as lithium aluminium hydride[174]. Recently, Gladysz and co-workers[175] demonstrated reduction of $Co_2(CO)_8$ by trialkylborohydrides. Octacarbonyldicobalt is reduced to tetracarbonylcobaltate(1-) under the influence of alkali metal amalgams[176].

Whereas direct reduction is attractive in that it offers, in theory, complete conversion of zerovalent cobalt to cobalt in the uni-negative state, drawbacks do exist. The preparation of alkali metal amalgams can be hazardous: Amalgams and hydride reducing agents can be difficult, or even dangerous, to handle. In addition to these considerations, the direct reduction methods may be susceptible to undesired side reactions. For example, mercury reacts with dicobalt octacarbonyl in the presence of sodium to give the trinuclear species, mercury bis-(tetracarbonylcobaltate)[177]. (It should be said that this problem may be avoided by performing the reduction using the pure alkali metal: Lithium wire has been employed.)[178]

Hydridotetracarbonylcobalt(I), $HCo(CO)_4$, is implicated in the formation of tetracarbonylcobaltate(1-) from octacarbonyldicobalt by hydride reducing agents[175]. $HCo(CO)_4$ is an undesired species

not only because of its toxicity but also because it can interfere with reactions later in the synthetic pathway. For example, $HCo(CO)_4$ reacts with acyl cobalt tetracarbonyls, $RCOCo(CO)_4$, to give aldehydes[39].

Lewis-base induced valence disproportionation of cobalt carbonyls to $Co(CO)_4^-$ and divalent cobalt species has been postulated by Wender, Sternberg and Orchin[179] to explain earlier findings by Hieber[21]. The method has recently been extended into hydrocarbon solvents by using phase-transfer disproportionating agents[163,180].

Wender, Sternberg and Orchin envisaged attack on octacarbonyldicobalt by the disproportionating base, B, as a nucleophilic displacement reaction. The leaving group in this process being the tetracarbonylcobaltate anion;

$$B + Co_2(CO)_8 \longrightarrow BCo(CO)_4^+ + Co(CO)_4^- \quad (18)$$

In some cases, the Co(I) product of process (18) is stable enough to be detected. This is especially true where B has the ability to stabilise low-valent metal. For example, the salt $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$, produced by attack of triphenylphosphine on octacarbonyldicobalt is well known. In these cases, a subsequent symproportionation step may occur to yield zerovalent dimers such as $Co_2(CO)_6(PPh_3)_2$[181].

Otherwise, $BCo(CO)_4^+$ rapidly undergoes a second valence disproportionation reaction to give a zerovalent cobalt moiety, presumably bound to carbon monoxide, and a divalent cobalt species which does not bear co-ordinated carbonyl groups. The produced zerovalent cobalt is, of course, susceptible to further attack by

B leading, eventually, to complete disproportionation to tetracarbonylcobaltate(1-) and divalent cobalt. Wender, Sternberg and Orchin do not offer any precise mechanism for the disproportionation of $BCo(CO)_4^+$ to divalent- and zerovalent-cobalt.

According to the overall equation for the process,(19),

$$^3/2\ Co_2(CO)_8 + 2B \longrightarrow 2Co(CO)_4^- + Co^{2+} + 2B + 4CO \quad -(19)$$

one third of the starting $Co_2(CO)_8$ is lost as divalent cobalt. Despite this, valence disproportionation offers the attraction that this reaction can be carried out under mild conditions. Hieber has shown that $Co_2(CO)_8$ can be disproportionated by using tetrahydrofuran as the disproportionating base, B, and conveniently, as solvent[182].

SECTION TWO : HALIDE INDUCED VALENCE DISPROPORTIONATION OF COBALT CARBONYLS IN ETHEREAL SOLVENTS

In accord with the findings of Hieber[182] that amines bring about valence disproportionation of cobalt carbonyls, it was found that N-methyl-2-pyrrolidone,N,N,N′,N′-tetramethylethylenediamine and N-methylmorpholine, rapidly and efficiently bring about the reaction. Attempts to use solutions of tetracarbonylcobaltate(1-) formed by this method in the synthesis of acyl cobalt tetracarbonyl from acyl halides resulted in reaction between the acyl halide and the amine to give the acyl ammonium halide. There is no evidence to suggest that complexed amines react in this manner. It is difficult, however, to guarantee the absence of free amine in these solutions.

Tetrahydrofuran has been shown to bring about valence

disproportionation of cobalt carbonyls[182], and this base may conveniently also be used as solvent for the disproportionation and for subsequent reactions of the product anion. Heck [183] has shown that acylcobalt tetracarbonyl may be formed by addition of acyl halides to ethereal solutions of tetracarbonylcobaltate(1-).

Attempts to repeat these reactions in ethyleneglycol dimethyl ether (glyme), diethyleneglycol dimethyl ether (diglyme) and tetrahydrofuran (THF) were obstructed by the reaction between the ether and the acyl halide. For example, iso-butyrylchloride reacts with THF to give δ-chloro-n-butyl iso-butyrate[184]. (The rates of these reactions are not, in general, too great to allow some acyl cobalt tetracarbonyl formation).

On several occasions, solutions of $Co_2(CO)_8$ in THF appeared not to give rise to tetracarbonylcobaltate(1-). Inspection of a number of sets of infrared spectra showed that when the initial concentration of $Co_2(CO)_8$ was high (above about 10^{-2} M in THF and glyme and above about 5×10^{-2} M in diglyme) little or no disproportionation is noted at ambient temperature. Instead, conversion to dodecacarbonyltetracobalt, $Co_4(CO)_{12}$, is preferred. At these high concentrations, $Co_4(CO)_{12}$ appears not to suffer significant valence disproportionation over a period of days.

An explanation of this behvaiour can be proffered by comparing Wender, Sternberg and Orchin's mechanism for valence disproportionation[179] with Ungváry and Markó's mechanism for the thermal conversion of $Co_2(CO)_8$ to $Co_4(CO)_{12}$[94,185]. Ungváry and Markó have shown that, whereas the inhibitory effect of released carbon monoxide depends on the solvent, the rate of formation of

$Co_4(CO)_{12}$ varies as the square of initial $Co_2(CO)_8$ concentration. They suggest that the formation of $Co_4(CO)_{12}$ can be explained in terms of the following scheme;

$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_{(8-n)} + nCO \quad \text{—— (20)}$$

n = 1 or 2

$$2\ Co_2(CO)_{(8-n)} \longrightarrow Co_4(CO)_{12} + xCO \quad \text{— (21)}$$

where n = 1, x = 2, where n = 2, x = 0

The establishment of the equilibrium or equilibria (20) is fast in comparison with (21), the rate determining step.

No rigorous study of the kinetics of the valence disproportionation of cobalt carbonyl has been reported. However, given the facts that the reaction between THF and $Co_2(CO)_8$ takes at least six hours to complete[182] and that no intermediates of this reaction have been observed, it would appear that attack by THF on $Co_2(CO)_8$ is the rate determining step. (This speculation can be supported by the observation that the rate of base induced valence disproportionation varies more or less with the classical nucleophilicity of the base). Bearing in mind that cobalt carbonyl is re-formed in a later stage of the reaction, the rate of valence disproportionation can be assumed to be, at most, first order in $Co_2(CO)_8$.

Thus, increasing the concentration of $Co_2(CO)_8$ will greatly enhance the rate of dimerisation compared with that of $Co(CO)_4^-$ formation.

The rate of valence disproportionation of $Co_4(CO)_{12}$ (22)

$$3/4\ Co_4(CO)_{12} \longrightarrow Co^{II} + 2\ Co(CO)_4^- + CO \quad \text{— (22)}$$

might be expected to be lower than that of valence disproportionation of $Co_2(CO)_8$ (19), on the grounds that the expulsion of the carbonyl anion from $Co_4(CO)_{12}$ requires the rupture of three metal-metal bonds, whereas, the analogous expulsion from $Co_2(CO)_8$ requires the breaking of only one cobalt-cobalt bond.

In some cases, the observed precipitation of some $Co_4(CO)_{12}$ may account in part for the reluctance to disproportionate.

An aliquot of sebacoyl chloride $ClOC(CH_2)_8COCl$ on addition to a THF solution containing tetracarbonylcobaltate(1-) and some unreacted dicobalt octacarbonyl caused an increase in the concentration of the anion! This unexpected, but reproducible, result led us to suspect that chloride anions released following nucleophilic attack by $Co(CO)_4^-$ on the acyl halide had acted as disproportionating agents.

A number of disproportionation reactions were carried out in ethereal solvents in the presence of various halides in order to test this assumption.

Salts of chloride, bromide and iodide were all found to significantly increase the rate of valence disproportionation of octacarbonyldicobalt and dodecacarbonyltetracobalt in THF, glyme and diglyme.

The co-cation is important mainly for its rôle in determining the solubility of the halide salt. Thus, transition metal halides (soluble in ethers), lithium halide (which is soluble in diglyme) and tetra-alkyl ammonium iodide are very effective catalysts for the

reaction.

In some cases, the cation may interfere with the course of the reaction. For example, octacarbonyldicobalt is converted to hydridotetracarbonylcobalt(I) in the presence of hydrochloric acid[183] This can be interpreted as halide induced valence disproportionation to tetracarbonylcobaltate(1-) and divalent cobalt (recognised by the bright blue colour produced in this reaction) followed by association of H^+ with $Co(CO)_4^-$ to give the hydrocarbonyl.

It can be foreseen that, in some cases, use of a metal halide as the disproportionating agent could lead to the formation of polynuclear metal complexes. The literature contains several references to the reactions between metal halides and salts of tetracarbonylcobaltate which give rise to products containing metal-cobalt bonds. For example, copper, silver[186] and thallium[187] halides react in this manner.

Addition of anhydrous cobaltous chloride to THF gives rise to an intense blue solution. This blue colour arises from the presence of the tetrachlorocobaltate (2-) anion. Inspection of the visible region electronic spectrum of these solutions shows that octahedrally co-ordinated cobalt (II) is also present. It seems likely that on dissolution in THF, process (23) occurs;

$$6THF + 2CoCl_2 \longrightarrow [Co(THF)_6][CoCl_4] \quad \text{——— (23)}$$

Cotton has pointed out[198] that halide ion dissociation from $CoCl_4^{2-}$ is very ready in complexing solvents. It seems likely, therefore, that free halide exists in THF solutions of $CoCl_2$ due to equilibria of the type (24).

$$CoCl_4^{2-} + THF \rightleftharpoons Co(THF)Cl_3^- + Cl^- \quad \text{——— (24)}$$

Indeed, it may be that octahedral and tetrahedral cobalt are interconvertible (25).

$$Co(THF)_6^{2+} + 4Cl^- \rightleftharpoons CoCl_4^{2-} + 6\ THF \quad \text{——— (25)}$$

Valence disproportionation of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ is significantly faster in THF solutions containing anhydrous cobaltous chloride than in pure THF.

An attempt to study this reaction more closely involved monitoring the intensities of the carbonyl stretching frequencies of various carbonyl species and interpreting these in terms of concentrations of the species.

Octacarbonyldicobalt concentration was estimated from the intensity of its absorption at 2040 cm^{-1}. The intensity of the bridging carbonyl stretch at 1843 cm^{-1} was found to be substantially affected by overlap from the 1884 cm^{-1} band of tetracarbonylcobaltate(1-). The band at 2055 cm^{-1} in the spectrum of $Co_4(CO)_{12}$ was assumed to indicate the concentration of this species. Again, the bridging carbonyl band at 1858 cm^{-1} was found to be substantially affected by intensity from the 1884 cm^{-1} band of $Co(CO)_4^-$. Presumably, intensity from the bridging carbonyl bands of neutral cobalt carbonyls affects the measured intensity at 1884 cm^{-1}. Since no other intense band is found in the spectrum of tetracarbonylcobaltate, however, intensity at 1884 cm^{-1} was taken as a guide to the concentration of $Co(CO)_4^-$. This fact should be borne in mind on considering the following results.

The half-height (absorbance scale) peak widths of the absorptions were measured in every case. The width of any band was found to vary very little from spectrum to spectrum, and so total

intensity was taken to be proportional to observed peak height.

Concentration is related to the intensity of an absorption by the Beer-Lambert law;

$$\log_{10} (I_o/I) = \varepsilon c l$$

where I_o is the intensity of the incident light, I is the intensity of the transmitted light, ε is the molar extinction co-efficient for a given band (in $l\ mol^{-1}\ cm^{-1}$) in the spectrum of a compound, c is the concentration of that compound (in mol. l^{-1}) and l is the length of the path of the beam through the solution (in cm.).

Since the intensities measured for the terminal carbonyl stretches for both $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are in fact compounded of two or more bands in each case, no value was assigned to the molar extinction co-efficients. Therefore, and because the same cell was used throughout, concentration of a given compound is represented by the quantity εcl.

In a preliminary experiment, a sample of $Co_4(CO)_{12}$ was allowed to stand in THF for two days. After this time, aliquots of anhydrous cobaltous chloride were added. Table 3 illustrates the decay of $Co_4(CO)_{12}$ and the formation of $Co(CO)_4^-$.

Table 3

t (hr. min.)	I_o	$Co_4(CO)_{12}$		$Co(CO)_4^-$		Comments
		I_{2055}	εcl	I_{1884}	$\varepsilon' xl$	
0,00	65.8	7.3	0.955	*	0	
51,00	66.1	9.2	0.856	37.0	0.252	0.05 g $CoCl_2$ added
51,03	65.1	11.4	0.757	23.8	0.437	
51,30	-	-	-	-	-	0.06 g $CoCl_2$ added
51,33	67.3	20.5	0.516	8.1	0.920	
52,00	-	-	-	-	-	0.5 g $CoCl_2$ added
52,03	68.4	31.5	0.337	4.0	1.23	
52,30	-	-	-	-	-	0.5 g $CoCl_2$ added
52,37	67.3	-	-	1.8	1.57	

Notes The process was carried out under 1 atmosphere of dried, oxygen free nitrogen at 25.0 $\pm$0.5 °C. ε is the molar extinction co-efficient for the 2055 cm^{-1} band of $Co_4(CO)_{12}$. ε' is the molar extinction co-efficient for the 1884 cm^{-1} band of $Co(CO)_4^-$, c is the concentration of $Co_4(CO)_{12}$ and x is the concentration of $Co(CO)_4^-$

These findings, illustrated in figure 12, clearly show that anhydrous cobaltous chloride significantly enhances the rate of valence disproportionation of $Co_4(CO)_{12}$ in THF.

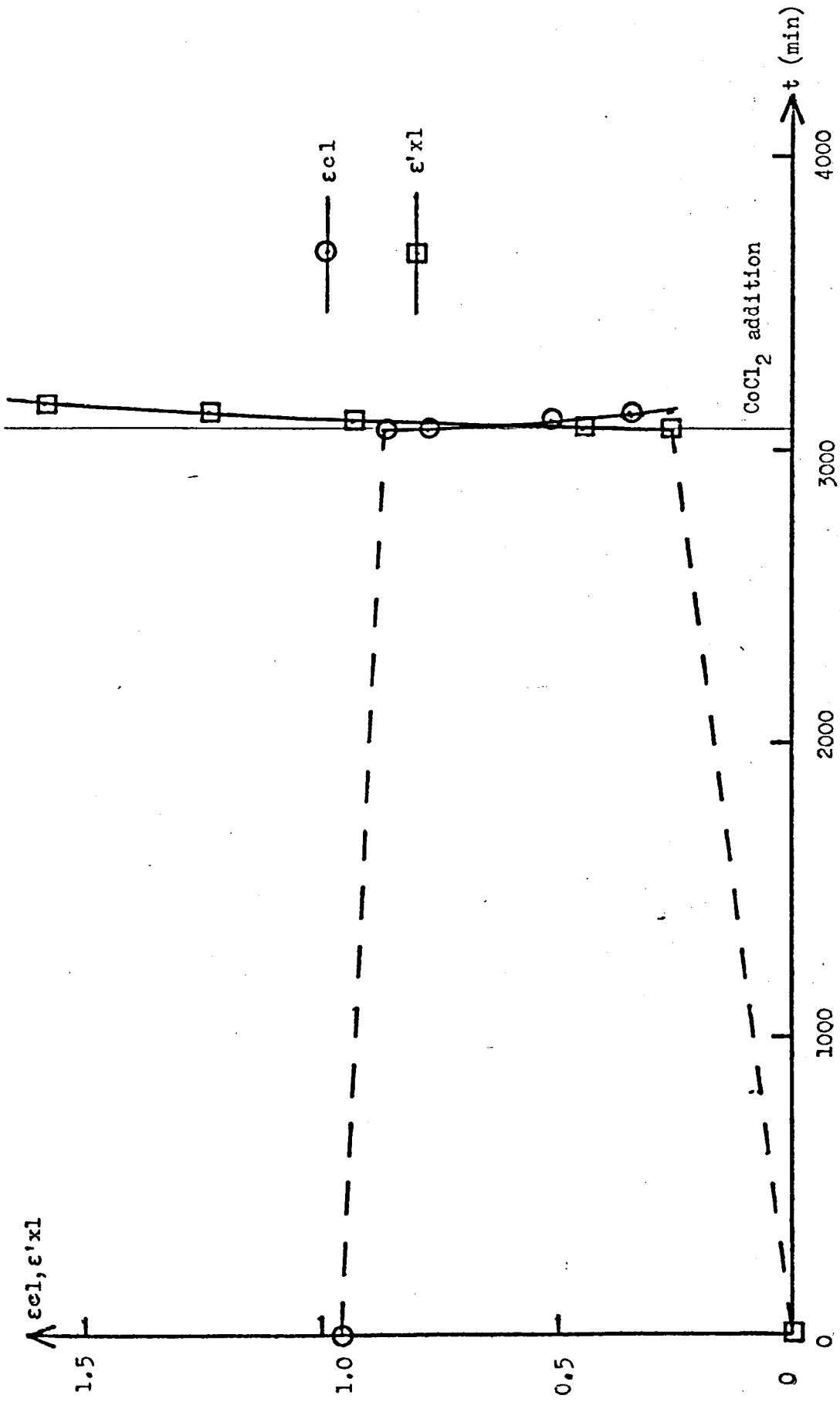


Figure 12: The decay of $Co_4(CO)_{12}$ and the formation of $Co(CO)_4^-$ in THF with time

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Prior to carrying out a more detailed investigation of the reaction, the effect of water on the rate of valence disproportionation of $Co_4(CO)_{12}$ was investigated: Addition of 1 ml water to a solution containing $Co_4(CO)_{12}$ in 9 ml THF caused immediate evolution of gas. After 15 minutes at room temperature, very little $Co_2(CO)_8$ was evident in the infrared spectrum of the reaction mixture. The mixture was pink. The effect of water can, therefore, by no means be neglected. Every effort was made to exclude this species, and reference experiments were carried out in parallel with the catalysed reactions to account for the effects of water.

The kinetics of the halide induced valence disproportionation of cobalt carbonyls in ethereal solvents do not comply with any simple rate law: Table 4 shows the effect of adding anhydrous cobaltous chloride to solutions of $Co_4(CO)_{12}$ in THF under one atmosphere of nitrogen at 25.0 $\pm$0.5 ^{o}C.

Table 4

a) $Co_4(CO)_{12}$ in the presence of 0.15 mM cobaltous chloride

t(min)	I_o	I_{2055}	εcl	I_{1884}	$\varepsilon' xl$	$\varepsilon' xl - \varepsilon' x_o l$
0	95.9	47.0	0.310	76.4	0.099	0
2.67	73.3	36.8	0.299	57.7	0.104	0.005
8.67	83.2	42.0	0.297	65.5	0.104	0.005
107	72.4	37.1	0.290	53.5	0.131	0.032
365	79.6	43.0	0.267	62.4	0.106	0.007
1251	78.2	45.7	0.233	49.6	0.198	0.099

b) $Co_4(CO)_{12}$ in the presence of 1.5 mM $CoCl_2$

t(min)	I_o	I_{2055}	εcl	I_{1884}	$\varepsilon' xl$	$\varepsilon' xl - \varepsilon' x_o l$
0	95.9	47.0	0.310	76.4	0.099	-
3.83	79.0	40.1	0.294	61.9	0.106	0.007
8.67	87.3	45.1	0.287	58.5	0.172	0.073
107	59.2	31.8	0.270	41.9	0.150	0.051
230	77.8	53.1	0.164	38.8	0.302	0.203
240	87.0	60.1	0.161	41.4	0.323	0.224
360	81.8	59.8	0.136	35.9	0.358	0.257
1240	76.0	*	-	22.9	0.521	0.422

Table 4 (contd.)

c) $Co_4(CO)_{12}$ in the presence of 15 mM $CoCl_2$

t(min)	I_o	I_{2055}	εcl	I_{1884}	$\varepsilon' xl$	$\varepsilon' xl - \varepsilon' x_o l$
0	95.9	47.0	0.310	76.4	0.099	-
2.83	66.2	41.4	0.203	36.9	0.254	0.155
13.33	79.2	55.2	0.157	39.8	0.299	0.200
25.83	84.7	57.3	0.170	33.0	0.409	0.310
105	72.7	*	-	19.0	0.583	0.484

Notes x_o is the concentration of $Co(CO)_4^-$ immediately prior to $CoCl_2$ addition. * implies no absorption.

Figure 13a illustrates the decay of $Co_4(CO)_{12}$ in this experiment, and figure 13b the formation of $Co(CO)_4^-$

The apparent oscillation in the concentration of $Co_4(CO)_{12}$ may or may not be spurious in this case. Note that the abnormally low $Co_4(CO)_{12}$ concentration after 13.33 minutes in 4c) is accompanied by a low value for $Co(CO)_4^-$ concentration. This could be taken to reflect some sampling error such as an incompletely filled cell.

There are cases, however, where an apparently anomolously low $Co_4(CO)_{12}$ concentration is not accompanied by an anomolously low value of $Co(CO)_4^-$ concentration. Table 5 and figure 14 illustrate this point.

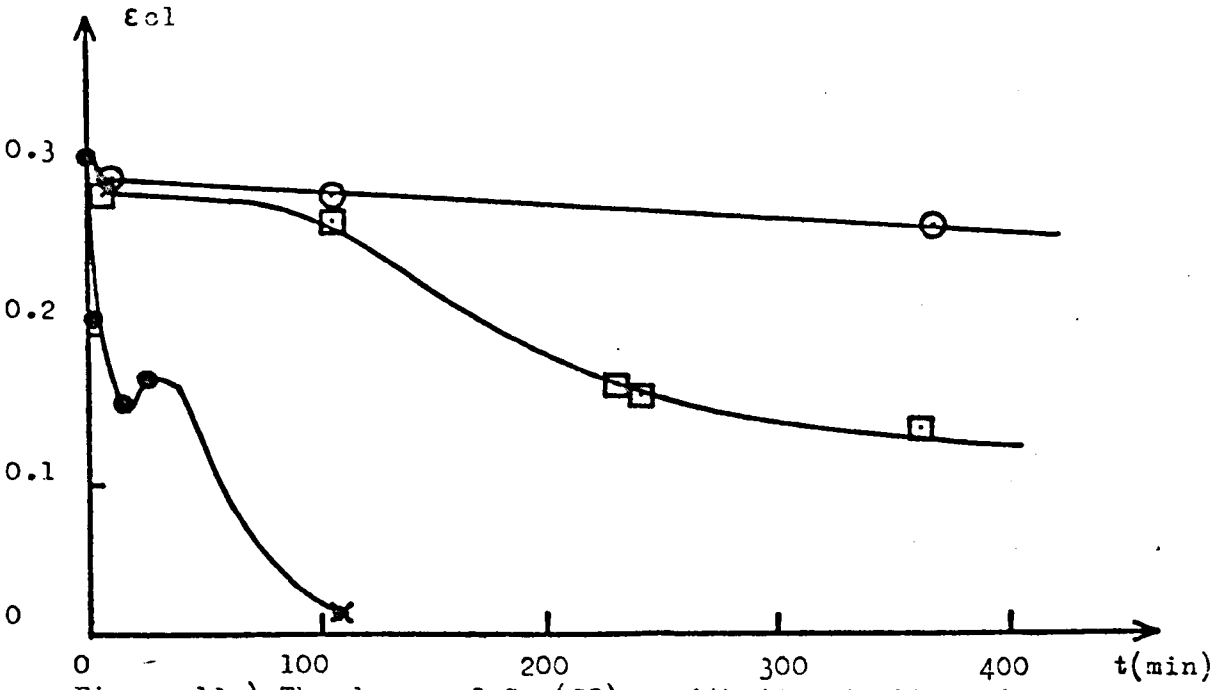

Figure 13a) The decay of $Co_4(CO)_{12}$ with time in THF under one atmosphere N_2 at 25.0 ± 0.5 °C in the presence of $CoCl_2$.

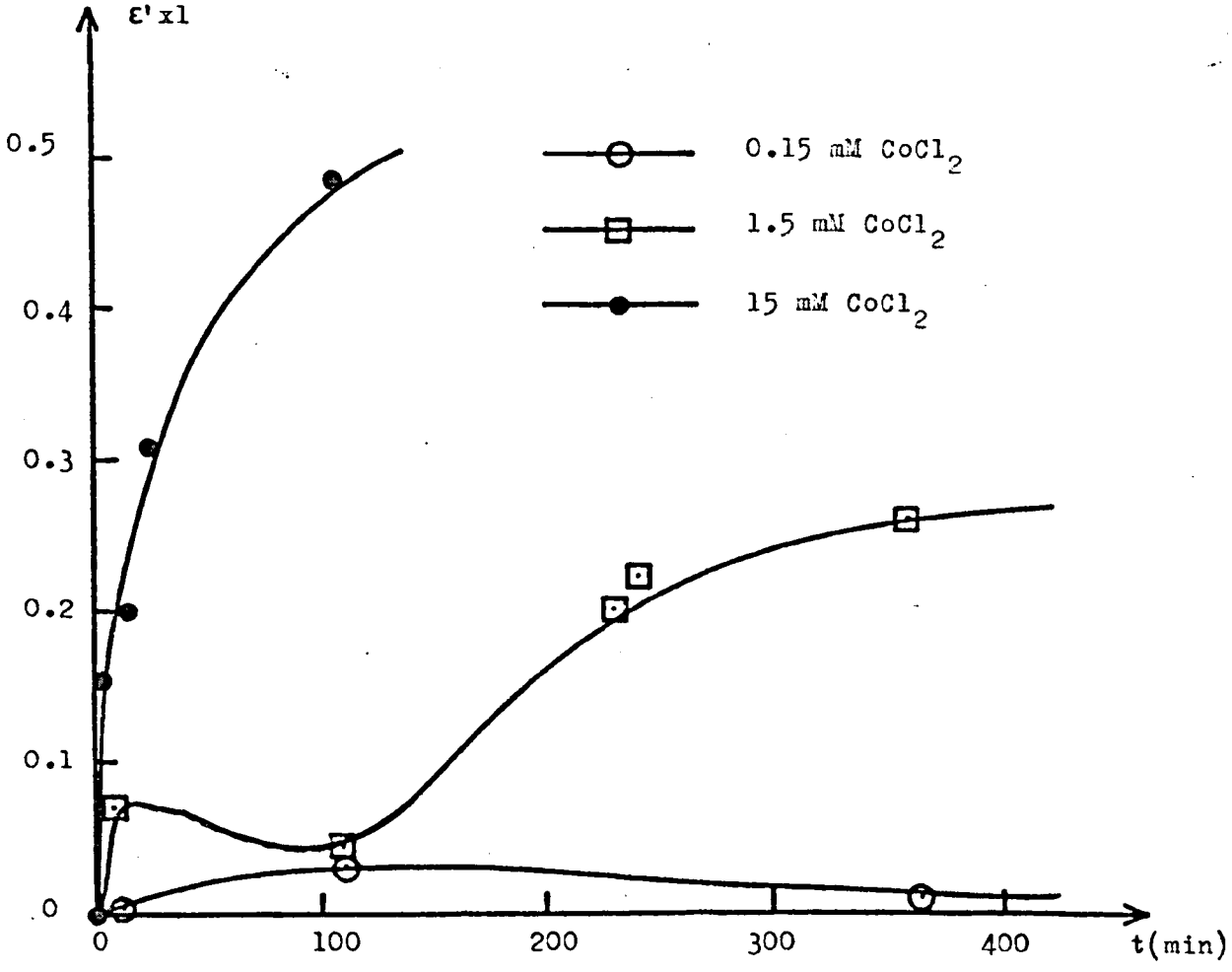

Figure 13b) The formation of $Co(CO)_4^-$ as in figure 13a).

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Table 5: The valence disproportionation of $Co_4(CO)_{12}$ in the presence of $CoCl_2$ in THF under 1 atmosphere nitrogen at 25.0 ±0.5 °C

a) $[CoCl_2] = 5.78 \times 10^{-4}$ M

t(min)	I_o	I_{2055}	εcl	I_{1884}	$\varepsilon' xl$	$\varepsilon' xl - \varepsilon' x_o l$
0	78.2	27.1	0.460	53.2	0.167	-
2.83	79.2	29.1	0.435	50.8	0.193	0.026
11.83	78.2	30.1	0.415	47.1	0.220	0.053
79	79.6	29.8	0.427	46.5	0.233	0.066
229	78.3	32.5	0.382	44.1	0.249	0.082

b) $[CoCl_2] = 1.6 \times 10^{-3}$ M

t(min)	I_0	I_{2055}	εcl	I_{1884}	$\varepsilon' xl$	$\varepsilon' xl - \varepsilon' x_o l$
0	78.2	27.1	0.460	53.2	0.167	-
3.67	79.6	30.1	0.422	49.3	0.208	0.041
14	77.6	29.8	0.415	45.8	0.229	0.062
86.17	89.4	32.5	0.439	48.3	0.267	0.100
230	88.7	32.8	0.432	45.4	0.291	0.124

c) $[CoCl_2] = 5.78 \times 10^{-3}$ M

t(min)	I_0	I_{2055}	εcl	I_{1884}	$\varepsilon' xl$	$\varepsilon' xl - \varepsilon' x_o l$
0	78.2	27.1	0.460	53.2	0.167	-
2	89.4	34.7	0.411	53.5	0.223	0.056
13	88.8	52.7	0.227	34.8	0.406	0.240
19.67	89.4	*	-	18.8	0.677	0.510

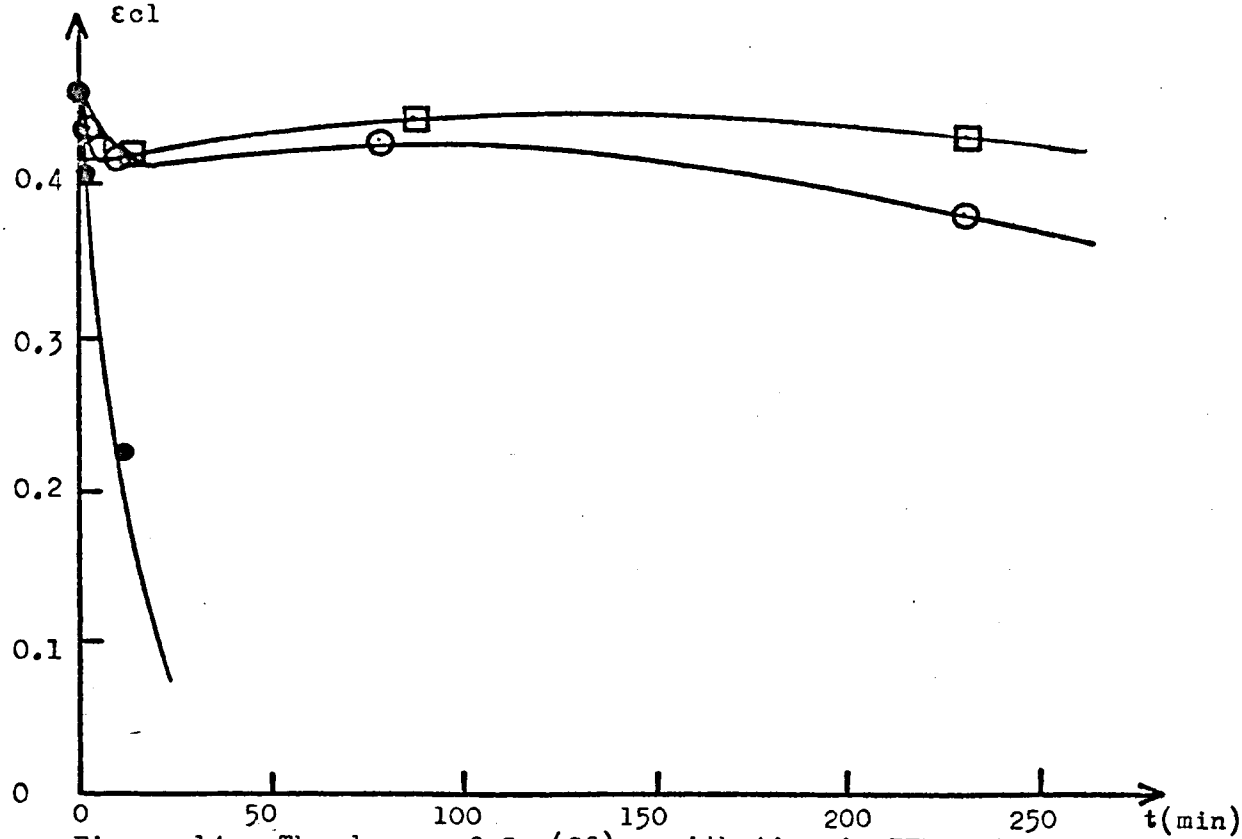

Figure 14a: The decay of $Co_4(CO)_{12}$ with time in THF under one atmosphere N_2 at 25.0 ± 0.5 °C in the presence of $CoCl_2$.

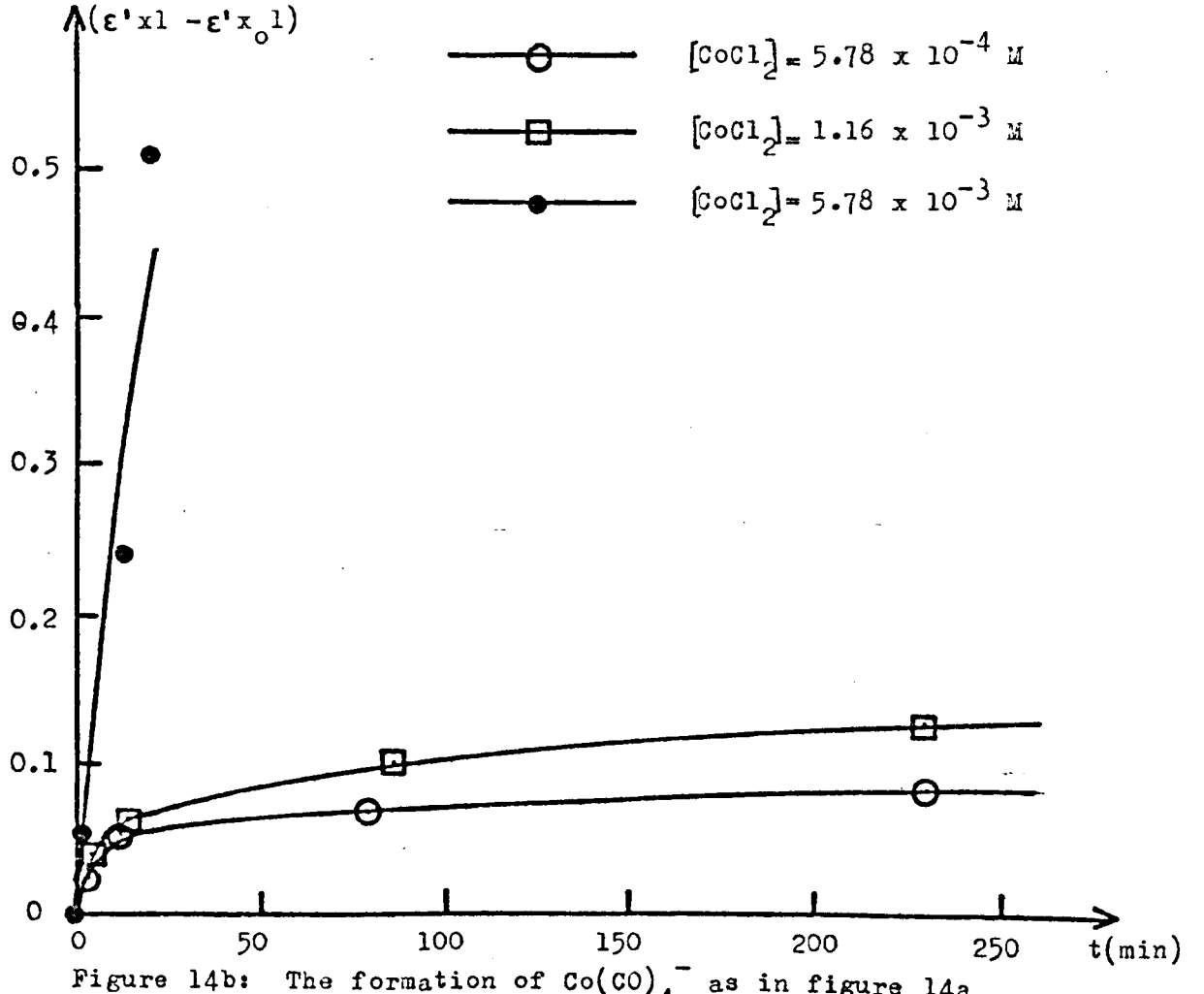

Figure 14b: The formation of $Co(CO)_4^-$ as in figure 14a

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Octacarbonyldicobalt is disproportionated more rapidly in THF solutions containing anhydrous cobaltous chloride than in pure THF. Again, however, the kinetics of the process are not straightforward. Indeed, $Co_2(CO)_8$ shows more marked oscillatory behaviour than does $Co_4(CO)_{12}$. Table 6 and figure 15 illustrate this point.

Table 6: The valence disproportionation of $Co_2(CO)_8$ in THF under 1 atmosphere nitrogen at 25.0 $\pm$ 0.5 ^{o}C in the presence of $CoCl_2$.

a) $[Co_2(CO)_8]$ = 4.37 x 10^{-2} M, $[CoCl_2]$ = 1.96 x 10^{-2} M

t(min)	I_o	I_{2040}	$\varepsilon c1$	I_{1884}	$\varepsilon x1$
0	74.9	3.8	1.295	-	-
2	73.3	8.9	0.916	28.0	0.418
17	73.9	19.9	0.570	14.6	0.704
32	76.0	17.5	0.638	12.7	0.777
35	71.8	16.9	0.628	12.4	0.763
68	71.2	21.8	0.514	12.8	0.745
101	74.4	†	-	11.3	0.818
303	74.2	-	-	6.2	1.078
1220	72.0	-	-	4.0	1.255

b) $[Co_2(CO)_8] = 2.46 \times 10^{-2}$ M, $[CoCl_2] = 2.32 \times 10^{-2}$ M

t(min)	I_o	I_{2040}	εcl	I_{1884}	$\varepsilon' xl$	$\varepsilon' xl - \varepsilon' x_o l$
0	72.1	12.7	0.754	55.7	0.112	-
3	72.2	22.7	0.510	30.3	0.377	0.265
15.5	71.4	18.6	0.584	15.0	0.678	0.566
28.5	72.4	23.1	0.496	12.4	0.766	0.654
74	70.8	30.1	0.371	6.3	1.051	0.939
149.5	72.9	36.0	0.306	6.0	1.085	0.973
1010	72.0	*	-	3.6	1.301	1.189

Notes. ε refers to the molar extinction co-efficient of $Co_2(CO)_8$ at 2040 cm^{-1}, c is the concentration of $Co_2(CO)_8$. † implies that substantial conversion to $Co_4(CO)_{12}$ is observed.

Neglecting this peculiarity in the decomposition of $Co_4(CO)_{12}$ and $Co_2(CO)_8$, it can be seen that the underlying trend is for the disproportionation to start rapidly and then to slow considerably. (The deceleration in the consumption of the carbonyls is more than can be accounted for by simple first or second order kinetics. Indeed, the order of the reaction appears to fall with time.) At low catalyst concentration, the reaction appears to cease altogether after a time, leaving considerable residual $Co_4(CO)_{12}$ or $Co_2(CO)_8$. Although it is impossible to quantify the effect, it appears that the increase in the rate with increasing catalyst concentration is too great to be accounted for by a linear relationship between the two. (This is particularly evident in figure 14.)

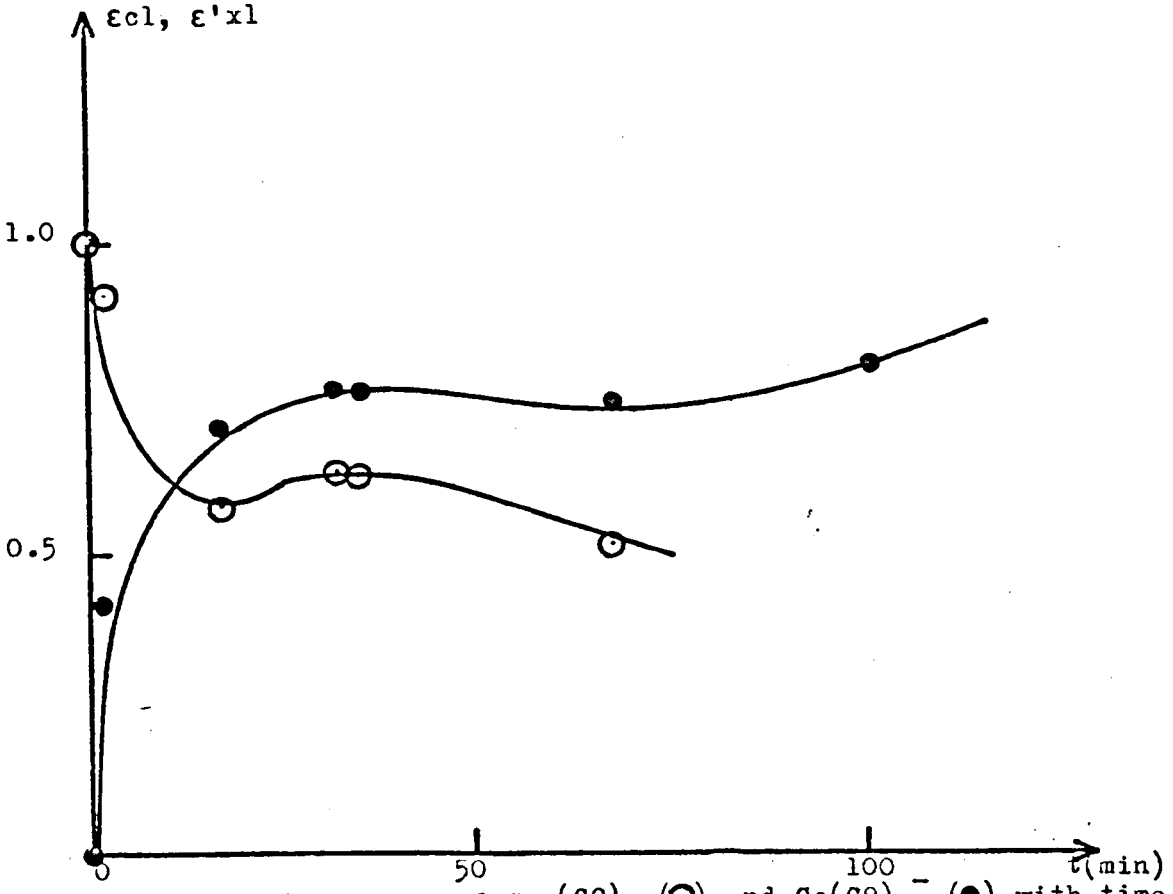

Figure 15a: The conc. of $Co_2(CO)_8$ (○) and $Co(CO)_4^-$ (●) with time during the disproportionation of a 43.7 mM soln. of $Co_2(CO)_8$ in the presence of 19.6 mM $CoCl_2$ in THF at 25.0 ± 0.5 °c under 1 atm. CO

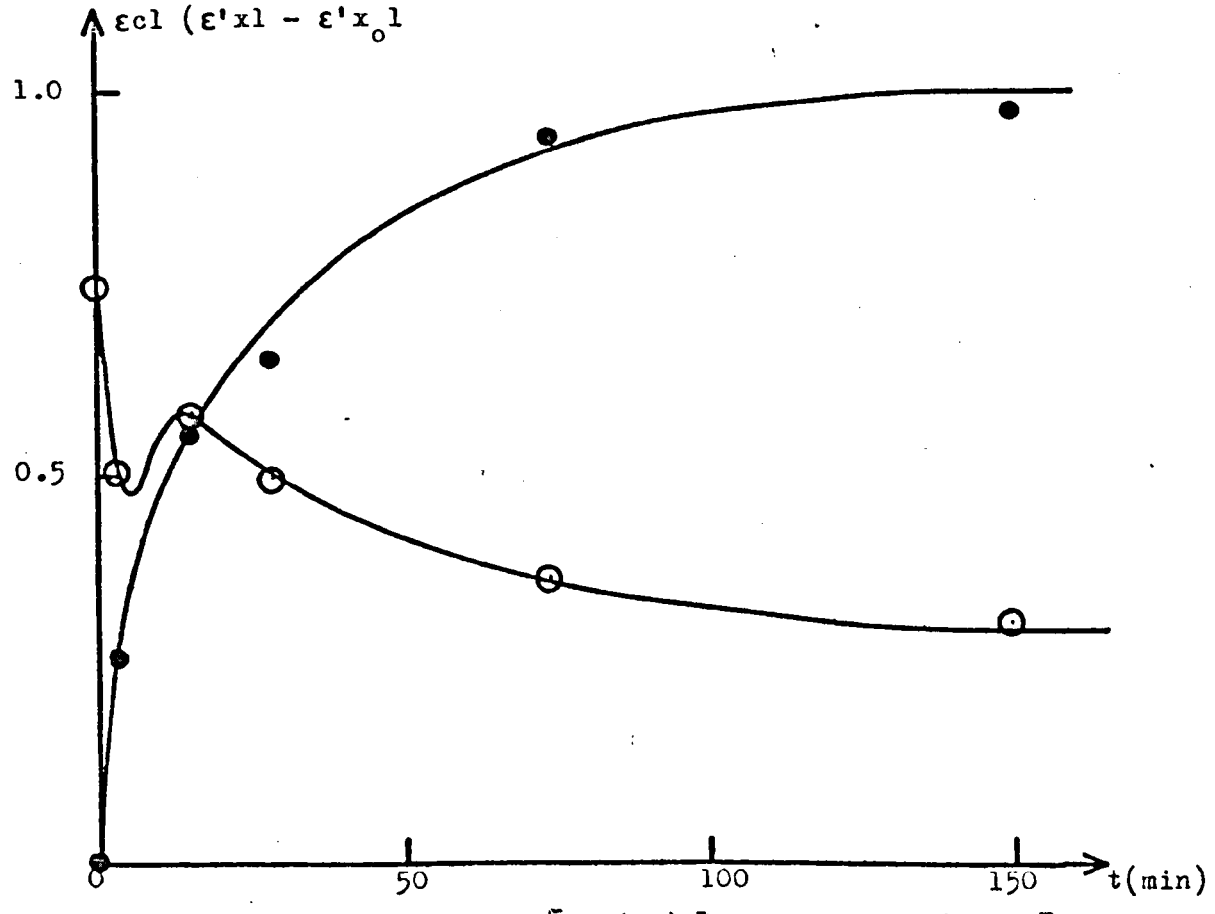

Figure 15b: As figure 15a: $[Co_2(CO)_8]_{init}$ = 24.6 mM, $[CoCl_2]_{init}$ = 23.2 mM

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This behaviour is consistent with some form of self-poisoning. If it is assumed that the true catalyst is the free halide anion, while the tetrahalocobaltate anion is a much poorer agent, then divalent cobalt production would poison the catalyst by complexing the free halide. (This assumption is supported by the absence of poisoning when Co^{II} is precipitated (vide infra).)

It is, unfortunately, impossible to test the effect of added divalent cobalt in this system, since addition of Co^{II} necessitates the addition of a counter-anion, such as acetate. This anion may in itself be a catalyst for the valence disproportionation reaction. Since the kinetics are so complex, it would be impossible to extricate the effect of the added anion from that of the added cation.

Carbon monoxide is produced in the reaction. It is quite conceivable that this species may have an inhibiting effect on the process. Table 7 and figure 16 compare the rate of valence disproportionation of $Co_4(CO)_{12}$ in the presence of roughly equivalent catalyst concentrations under atmospheres of nitrogen and carbon monoxide.

Table 7 a): The valence disproportionation of 3.0×10^{-2} M $Co_4(CO)_{12}$ in the presence of 9.8×10^{-3} M $CoCl_2$ in THF under 1 atmosphere N_2 at $25.0 \pm 0.5\ ^{0}C$

t(min)	I_o	I_{2055}	εcl
0	77.1	15.6	0.694
3.08	77.0	17.9	0.634
13.25	78.1	27.6	0.452
23	76.6	38.9	0.294

Table 7 b): The valence disproportionation of 3.0×10^{-2} M $Co_4(CO)_{12}$ in the presence of 8.8×10^{-3} M $CoCl_2$ under 1 atmosphere carbon monxide at 25.0 ± 0.5 °C.

t(min)	I_o	I_{2055}	εcl
0	75.3	15.2	0.695
2.67	72.9	16.0	0.659
13.67	72.0	20.2	0.552
25	72.8	23.0	0.500
47	73.3	**	-

** Indicates the formation of a substantial quantity of $Co_2(CO)_8$.

Carbon monoxide inhibition of the valence disproportionation reaction seems to be significant: It is impossible to extract from this result any quantification of the inhibiting effect. Carbon monoxide inhibition implies that at least one carbonylgroup is lost from the cobalt carbonyl prior to, or during, the rate determining step.

Octacarbonyldicobalt formation from dodecacarbonyltetracobalt was noted in all cases where the disproportionation was attempted under 1 atmosphere of carbon monoxide. In a few cases, where cobaltous chloride concentration was high, $Co_4(CO)_{12}$ was converted to $Co_2(CO)_8$ in the absence of an applied carbon monoxide atmosphere. It could be argued that rapid valence disproportionation in these cases led to a fairly high partial pressure of the gas.

In the absence of added cobaltous chloride, a solution of $Co_4(CO)_{12}$ appears to undergo a small degree of conversion to $Co_2(CO)_8$.

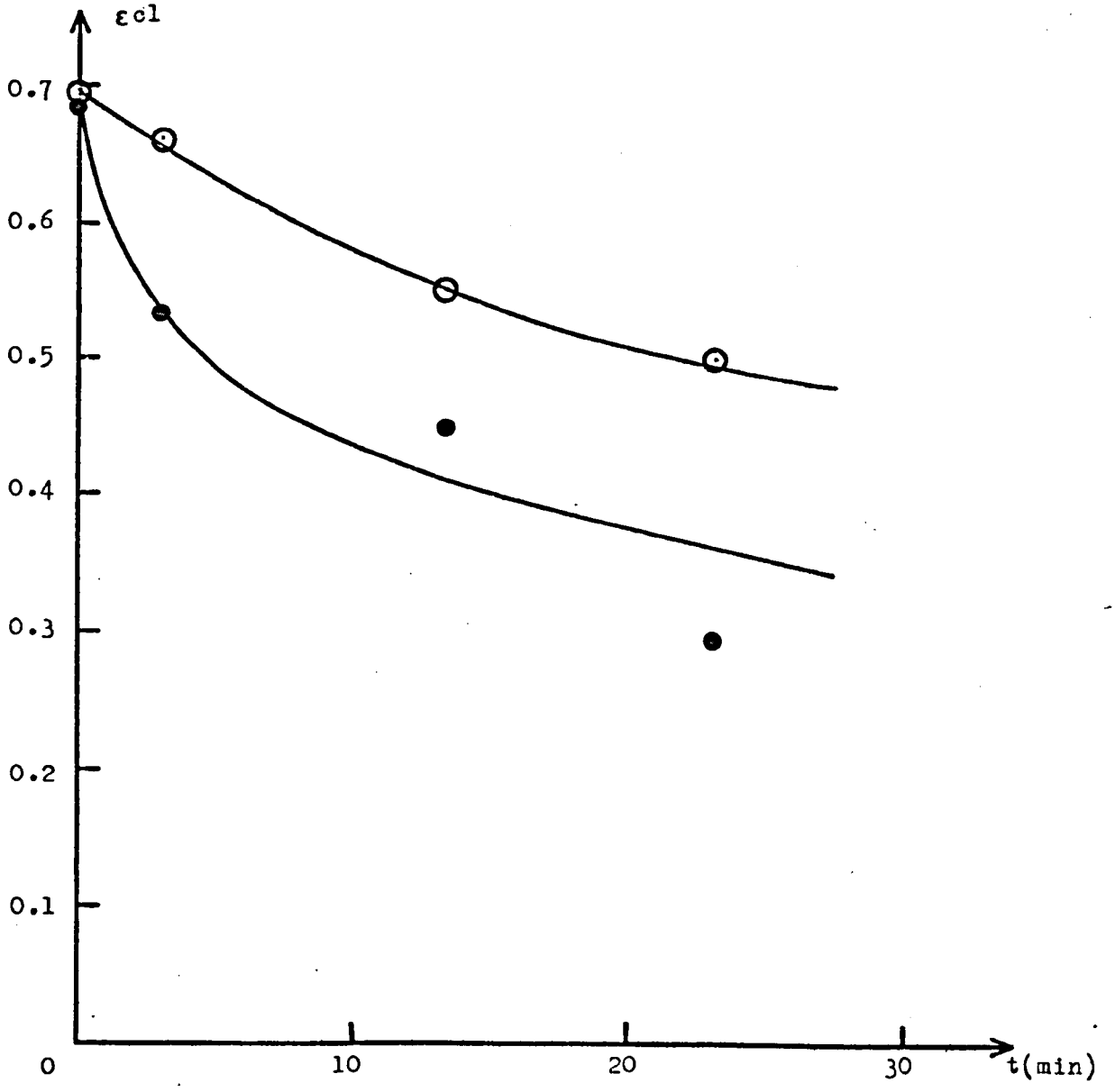

Figure 16: The decay of $Co_4(CO)_{12}$ with time in THF at 25.0 ± 0.5 °C

—●— in the presence of 9.8×10^{-3} M $CoCl_2$ under 1 atm. N_2

—○— in the presence of 8.8×10^{-3} M $CoCl_2$ under 1 atm. CO

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This is illustrated in figure 17 in terms of change of line shape in the carbonyl region of the infrared spectra.

The conversion of $Co_4(CO)_{12}$ to $Co_2(CO)_8$ further confounds attempts to study the kinetics of valence disproportionation of $Co_4(CO)_{12}$ under carbon monoxide.

The application of 1 atmosphere of hydrogen does not appear to alter the course of the reaction. At no stage was any $HCo(CO)_4$ detected during the valence disproportionation of $Co_4(CO)_{12}$ by $CoCl_2$ in THF.

No attempt was made to quantify the effect of the presence of 1 atmosphere of hydrogen on the rate of the process. The reaction can be made to proceed rapidly in the presence of high catalyst concentrations: For example, a 1.5×10^{-2} M solution of $Co_4(CO)_{12}$ in THF was fully disproportionated by 1.3×10^{-2} M anhydrous cobaltous chloride in under 2 hr. at 25.0 ± 0.5 °c under one atmosphere of hydrogen. At this pressure, hydrogen quite probably affords an inert atmosphere for the reaction.

In summary, it may be said that halide induced valence disproportionation of cobalt carbonyls in THF is extremely kinetically complex. Consequently, no quantitave interpretation of the results has been attempted. The following observations can, however, be made: Anhydrous cobaltous chloride increases the rate of valence disproportionation of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in THF. The reaction slows considerably with time indicating that the catalyst may be poisoned by some product of the reaction, perhaps divalent cobalt. The application of one atmosphere of carbon monoxide significantly

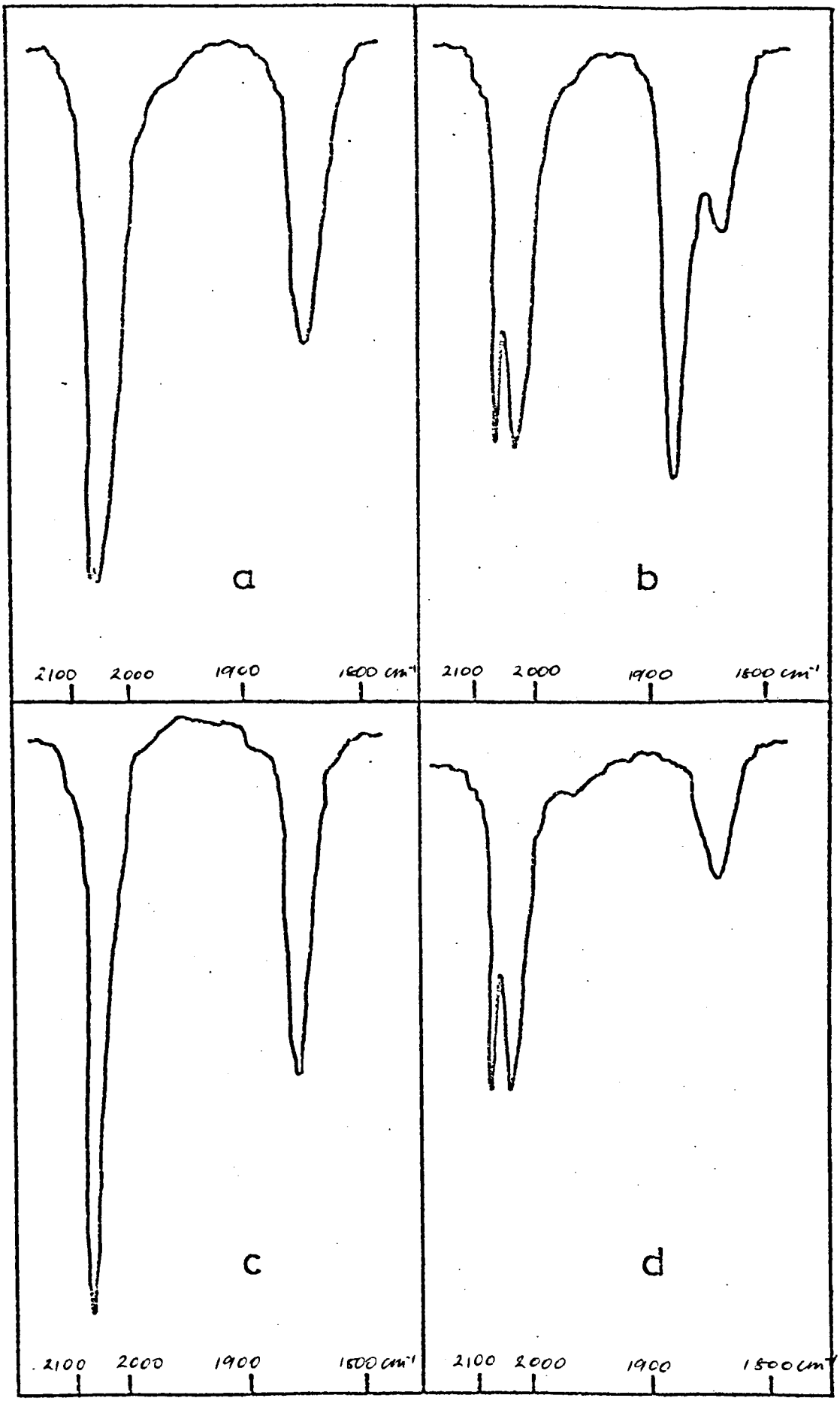

Figure 17 a) $Co_4(CO)_{12}$ in THF after 19 hrs. at R.T. under 1 atm. CO
b) $Co_4(CO)_{12}$ in THF in the presence of 8.8×10^{-3} M $CoCl_2$ after one hr. at R.T. under 1 atm. CO
c) $Co_4(CO)_{12}$ in THF
d) $Co_2(CO)_8$ in THF

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slows the disproportionation reaction. The application of one atmosphere of hydrogen does not affect the course of the reaction. Anhydrous cobaltous chloride allows the valence disproportionation of $Co_2(CO)_8$ to proceed where otherwise (page 47), only, or chiefly, conversion to $Co_4(CO)_{12}$ would be observed. Anhydrous cobaltous chloride assists the conversion of $Co_4(CO)_{12}$ to $Co_2(CO)_8$ in the presence of carbon monoxide.

Tetracarbonylcobaltate(1-) has been shown[102] to react with $Co(B)_6^{2+}$, where B is a weakly co-ordinated ligand, to give the neutral carbonyl deficient species, hexadecacarbonylhexacobalt. Octacarbonyltricobalt is a proposed intermediate in this process. It is not inconceivable that this intermediate could pick up carbon monoxide (as does hexadecacarbonylhexacobalt[114]) to give octacarbonyldicobalt or dodecacarbonyltetracobalt depending on the prevailing conditions. Thus, a plausible mechanism for the regeneration of $Co_4(CO)_{12}$ exists:

$$^3/_4\ Co_4(CO)_{12} \longrightarrow 2\ Co(CO)_4^- + "Co^{II}" + CO \quad \text{—— (26)}$$

$$"Co^{II}" + 6\ THF \longrightarrow Co(THF)_6^{2+} \quad \text{—— (26a)}$$

$$2\ Co(CO)_4^- + Co(THF)_6^{2+} \longrightarrow Co_3(CO)_8 + 6\ THF \quad \text{—— (27)}$$

$$Co_3(CO)_8 + CO \longrightarrow {}^3/_4\ Co_4(CO)_{12} \quad \text{—— (28)}$$

Step (27) is, in fact, a composite of two steps;

$$Co(THF)_n^{2+} + Co(CO)_4^- \longrightarrow \{Co_2(CO)_4(THF)_n\}^+ \quad \text{—— (27a)}$$

$$\{Co_2(CO)_4(THF)_n\}^+ + Co(CO)_4^- \longrightarrow Co_3(CO)_8 + n\,THF \quad \text{—— (27b)}$$

It is proposed that (27a) or (27b) is rate determining in the regeneration of $Co_4(CO)_{12}$: That is, $Co_3(CO)_8$ picks up CO extremely rapidly. Equations (27) and (28) can then be combined to give (29);

$$2\ Co(CO)_4^- + Co(THF)_6 + CO \longrightarrow {}^3/_4\ Co_4(CO)_{12} + 6THF \quad \text{—— (29)}$$

(29) is the reverse of (26): Thus the valence disproportionation of $Co_4(CO)_{12}$ in THF is expected to be reversible. (The argument extends to other weakly co-ordinating solvents in which the $Co^{II}/Co(CO)_4^-$ system is soluble.)

In the absences of halides, the $Co_4(CO)_{12}$ /THF system would be expected to approach equilibrium in the usual (non-oscillatory) manner. When chloride is present, however, the forward reaction in process (30) is catalysed.

$$^3/4\ Co_4(CO)_{12} + 6\ THF \xrightleftharpoons{(Cl^-)} 2\ Co(CO)_4^- + Co(THF)_6^{2+} + CO \quad \text{—(30)}$$

$Co(THF)_6^{2+}$ and $4Cl^-$ combine to give tetrachlorocobaltate(II) according to equation (25′);

$$Co(THF)_6^{2+} + 4\ Cl^- \rightleftharpoons CoCl_4^{2-} + 6\ THF \quad \text{———} \quad (25')$$

(Note that the symbol, $\rightleftharpoons$ in equations (30) and (25′) indicates that these reactions are reversible, it is not intended to imply that equilibrium is reached.)

The formation of $Co(THF)_6^{2+}$ in (26), in addition to increasing the rate of the reverse reaction in (30) as in normal equilibration, also inhibits the forward process by removing the *free halide*.

The above describes a negative feedback loop: A feedback loop is a requirement of oscillatory processes[189].

This treatment represents a drastic oversimplification: It has taken no account of dissociations of the type (24):

$$CoCl_4^{2-} + THF \rightleftharpoons [CoCl_3(THF)]^- + Cl^- \quad \text{———} \quad (24)$$

Divalent cobalt produced in (26) has been taken to be 'naked' Co^{II}. This is almost certainly untrue, but this approximation is unlikely to be serious, since (25′) represents a series of reversible

reactions involving mixed THF-chloride complexes of Co^{II} ((24) is one of these processes.) "Co^{II}" is likely to be one of these mixed complexes.

No account has been taken of the relative rates of reactions (26) and (29). The observation of an oscillation, and the characteristics of the oscillatory behaviour will depend on this factor as well as on the initial concentrations of dodecacarbonyltetracobalt and cobaltous chloride.

The argument applies equally to $Co_2(CO)_8$ and $Co_4(CO)_{12}$. Whether regenerated cobalt carbonyl appears as $Co_4(CO)_{12}$ or as $Co_2(CO)_8$ will depend on the amount of CO present. It is difficult to distinguish between $Co_4(CO)_{12}$ formation from $Co_2(CO)_8$ by the above route and $Co_4(CO)_{12}$ formation by thermal dimerisation of $Co_2(CO)_8$. The above route does, however, explain the observed formation of $Co_2(CO)_8$ from $Co_4(CO)_{12}$ in the presence of carbon monoxide.

Other halides bring about valence disproportionation of cobalt carbonyls in various solvents. The limiting factor is the solubility of the halide salt, and perhaps of the product tetracarbonylcobaltate salt in the solvent concerned. For example, lithium chloride was found to bring about very rapid valence disproportionation of $Co_4(CO)_{12}$ in diglyme. Tetra-n-butylammonium iodide was found to disproportionate $Co_2(CO)_8$ in THF.

The applicability of halide catalysed valence disproportionation as part of a synthetic scheme was demonstrated by the formation of (trihapto-allyl)-tricarbonylcobalt(I) from allyl bromide and $Co_2(CO)_8$ in THF[190] in the presence of anhydrous cobaltous chloride.

$Co_2(CO)_8$ (1.55 mmole) reacted completely with allyl bromide (2.35 mmole) in about 3 hours at room temperature to give allyl cobalt tricarbonyl.

SECTION THREE : HALIDE INDUCED VALENCE DISPROPORTIONATION OF COBALT CARBONYLS IN HYDROCARBON SOLVENTS

Halide catalysed valence disproportionation of cobalt carbonyls may be extended to hydrocarbon solvents by employing salts of 'crown' complexed cations, many of which are known[191] to be soluble in such solvents.

(The crown ether used in all cases in this work was 2, 5, 8, 15, 18, 21 - hexaoxatricyclo $[20.4.0.0^{9,14}]$ hexacosane. This will be referred to as dicyclohexyl-18-crown-6, or simply as 'crown').

The binary halides of alkali metal tend not to be amenable to solubilisation by crown ethers. In accord with this, solutions of cobalt carbonyls in toluene or benzene show no tendency to disproportionate in the presence of KCl, KBr or KI and dicyclohexyl-18-crown-6.

Potassium tetrahalocobaltate, K_2CoX_4 (X = Cl or Br) may however be brought into solution in benzene or toluene in the presence of this crown ether.

Valence disproportionation of octacarbonyldicobalt by $[K(\text{dicyclohexyl-18-crown-6})]_2\ CoX_4$ in benzene and toluene are slow in comparison with the reaction in THF catalysed by $CoCl_2$. For example, a solution containing 2.36 mmole $Co_2(CO)_8$ and 0.275 mmole $[K(\text{dicyclohexyl-18-crown-6})]_2\ CoBr_4$ in 50 ml toluene took

23.5 hours to reach 17 % completion. No further disproportionation took place over 25 hours. Note that given the stoichiometric reaction (31),

$$3/_2\ Co_2(CO)_8 + [K(crown)]_2CoBr_4 \longrightarrow 2[K(crown)]Co(CO)_4 + 2CoBr_2 + 4\ CO \quad \text{—— (31)}$$

0.275 mmoles of $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2\ CoBr_4$ should consume 0.413 mmoles $Co_2(CO)_8$, that is, 17.5 % of the $Co_2(CO)_8$ originally present.

It would appear that the reaction of $Co_2(CO)_8$ with crown complexed metal halides is stoichiometric. The infrared spectra of the reaction mixture shows a strong band at 1880 cm^{-1}, indicating that tetracarbonylcobaltate(1-) is maintained in solution. A blue or blue-green powder separates indicating that CoX_2 is precipitated.

The reason for the sluggishness of the reaction in hydrocarbon solvents may be taken as further evidence that CoX_4^{2-} is a much poorer catalyst than free X^-. (It seems likely that little, if any, free halide exists in solutions of tetrahalocobaltate in non-complexing solvents). Other conceivable factors should not, however, be neglected. For example, ion pairing and solvation energies,will vary on going from ethereal to hydrocarbon solvents. Insufficient information is available to assess the importance of these factors.

The fact that valence disproportionation is possible in hydrocarbon solvents, and in the complete absence of nitrogen- or oxygen- containing bases is important. Reactions of highly active organic halides with tetracarbonylcobaltate may now be brought about without side reaction between the halide and the solvents.

Although the disproportionation reaction is stoichiometric when considered in isolation, as part of a reaction scheme such as (32) it becomes catalytic in the crown-complexed potassium salt;

$$^{3}/_{2}\ Co_2(CO)_8 + [K(crown)]_2\ CoX_4 \longrightarrow 2[K(crown)][Co(CO)_4] + 2\ CoX_2 + 4\ CO$$

$$2\ [K(crown)][Co(CO)_4] + 2\ RX \rightarrow 2\ RCo(CO)_4 + 2[K(crown)]X$$

$$2[K(crown)]X + CoX_2 \longrightarrow [K(crown)]_2[CoX_4]$$

$$3/2\ Co_2(CO)_8 + 2\ RX \rightarrow 2\ RCo(CO)_4 + CoX_2 + 4\ CO \quad \text{——} \quad (32)$$

Dicyclohexyl-18-crown-6 does not react with potassium halide to give K(crown)X. This reluctance has been attributed[191] to the high lattice energy of potassium halide. There is no reason to suspect, however, that the salt K(dicyclohexyl-18-crown-6)X is kinetically unstable (with respect to decomplexation) under the conditions of this reaction.

It was found that anhydrous cobaltous chloride dissolves in toluene or benzene which contains dicyclohexyl-18-crown-6 to give a blue solution. The electronic spectrum of such a solution in the region 600 - 700 nm are quite similar to that of K_2CoCl_4 in the same solvents (see section 5). These blue solutions bring about extremely slow valence disproportionation of $Co_2(CO)_8$.

Tetra-n-butylammonium iodide, $(Bu^n)_4NI$, is soluble in hydrocarbon solvents and can, therefore be employed to bring about valence disproportionation of cobalt carbonyls in these media.

The divalent cobalt product of the reaction, CoI_2, is completely insoluble in these solvents. The reaction can be described as being stoichiometric in the halide, according to the reaction scheme (33)

$$2(Bu^n)_4NI + {}^3/2\ Co_2(CO)_8 \rightarrow CoI_2\downarrow + 2[(Bu^n)_4N][Co(CO)_4] + 4\ CO \quad - (33)$$

The reaction was studied in more detail by monitoring the disappearance of the carbonyl stretching frequencies of $Co_2(CO)_8$ in the infrared spectra,

The results of this investigation are summarised on table 8.

Table 8: The decay of $Co_2(CO)_8$ in toluene in the presence of $(Bu^n)_4NI$ under 1 atmosphere of carbon monoxide at 25.0 ± 0.5 °C

spectrum no.	I_o	I_{2040}	εcl	$\ln\left(\frac{c_o}{c}\right)$	t(min)
0A	87.8	68.0	0.111	0	0
0B	88.8	69.0	0.110	-	220
1A	88.1	72.2	0.086	0.255	10.0
1B	87.3	74.0	0.072	0.433	17.5
1C	88.0	78.8	0.050	0.780	34.0
1D	88.6	83.0	0.028	1.377	56.0
2A	88.9	74.3	0.078	0.353	14.5
2B	89.0	76.9	0.063	0.566	22.0
2C	88.8	78.8	0.052	0.758	31.0
2D	87.6	81.5	0.031	1.276	52.5
2E	*	-	-	-	84.0
3A	93.4	77.9	0.079	0.340	8.5
3B	88.7	79.1	0.050	0.780	20.5
3C	88.6	82.5	0.031	1.276	32.0
3D	88.3	84.0	0.022	1.618	40.5
3E	**	-	-	-	58.5

contd.

Table 8 (contd.)

spectrum no.	I_o	I_{2040}	εcl	$\ln\left(\frac{c_o}{c}\right)$	t(min)
4A	88.2	77.0	0.059	0.632	8.5
4B	88.2	82.9	0.027	1.414	23.0
4C	88.2	85.2	0.015	2.001	32.5
4D	**	-	-	-	87.5

Notes: 1) ε is the molar extinction co-efficient of $Co_2(CO)_8$ at 2040 cm^{-1}.

2) $[(Bu^n)_4NI]_{init}$ = 0 in spectra 0, 0.123 M in 1, 0.120 M in 2, 0.184 M in 3 and 0.306 M in 4.

3) * signifies a very low value of $[Co_2(CO)_8]$

** indicates no evidence of $Co_2(CO)_8$

The integral form of the first order rate law equates $\ln\frac{c_o}{c}$ with kt, where c is the concentration of a reactant at time, t and c_o is the initial concentration of this species. Values of $\ln\frac{c_o}{c}$ were calculated for each value of εcl, and these are listed in table 8.

$Ln\frac{c_o}{c}$ was plotted against time (figure 18) for each of the experiments in table 8. Figure 18 illustrates that when $[(Bu^n)_4NI]$ is very much greater than $[Co_2(CO)_8]$, the reaction between the two in toluene under 1 atmosphere of carbon monoxide obeys first order kinetics: That is, the reaction is first order in $Co_2(CO)_8$.

Table 9 and figure 19 show that the apparent rate constant , k, increases linearly with $(Bu^n)_4NI$ concentration. Since effectively no reaction occurred in the absence of the alkyl ammonium halide,

the value for k at $[(Bu^n)_4NI] = 0$ can be taken to be zero.

Table 9: The variation of apparent first order rate constant, k in the reaction between $Co_2(CO)_8$ and $(Bu^n)_4NI$ in toluene with $(Bu^n)_4NI$ concentration where $[(Bu^n)_4NI] \quad [Co_2(CO)_8]$

reaction no.	k x 10^2 (min^{-1})	$[(Bu^n)_4NI]$ ($mol.l^{-1}$)
0	0	0
1	2.41	0.123
2	2.41	0.120
3	3.96	0.184
4	6.40	0.306

It can be seen from figure 19 that where $[(Bu^n)_4NI] >> [Co_2(CO)_8]$, the rate of the reaction increases linearly with tetra-n-butylammonium iodide concentration. The slope of the graph indicates a dependence on $[(Bu^n)_4NI]$ of 0.21 $l.mol^{-1}$ min^{-1}, or 3.5×10^{-3} l. mol^{-1} sec^{-1}.

The following points may be deduced from these results:

1) When tetra-n-butylammonium iodide concentration is very much greater than that of $Co_2(CO)_8$, the reaction obeys first order kinetics. There is no evidence of poisoning as there is during CoX_2 catalysed valence disproportionation in THF. Since product Co^{II} is precipitated in the latter case, but not in the former, it seems reasonable to assume that Co^{II} is the catalyst poison in THF, and that poisoning takes the form of co-ordination of free halide to cobalt(II).
2) The kinetics of this system are well behaved. This means that

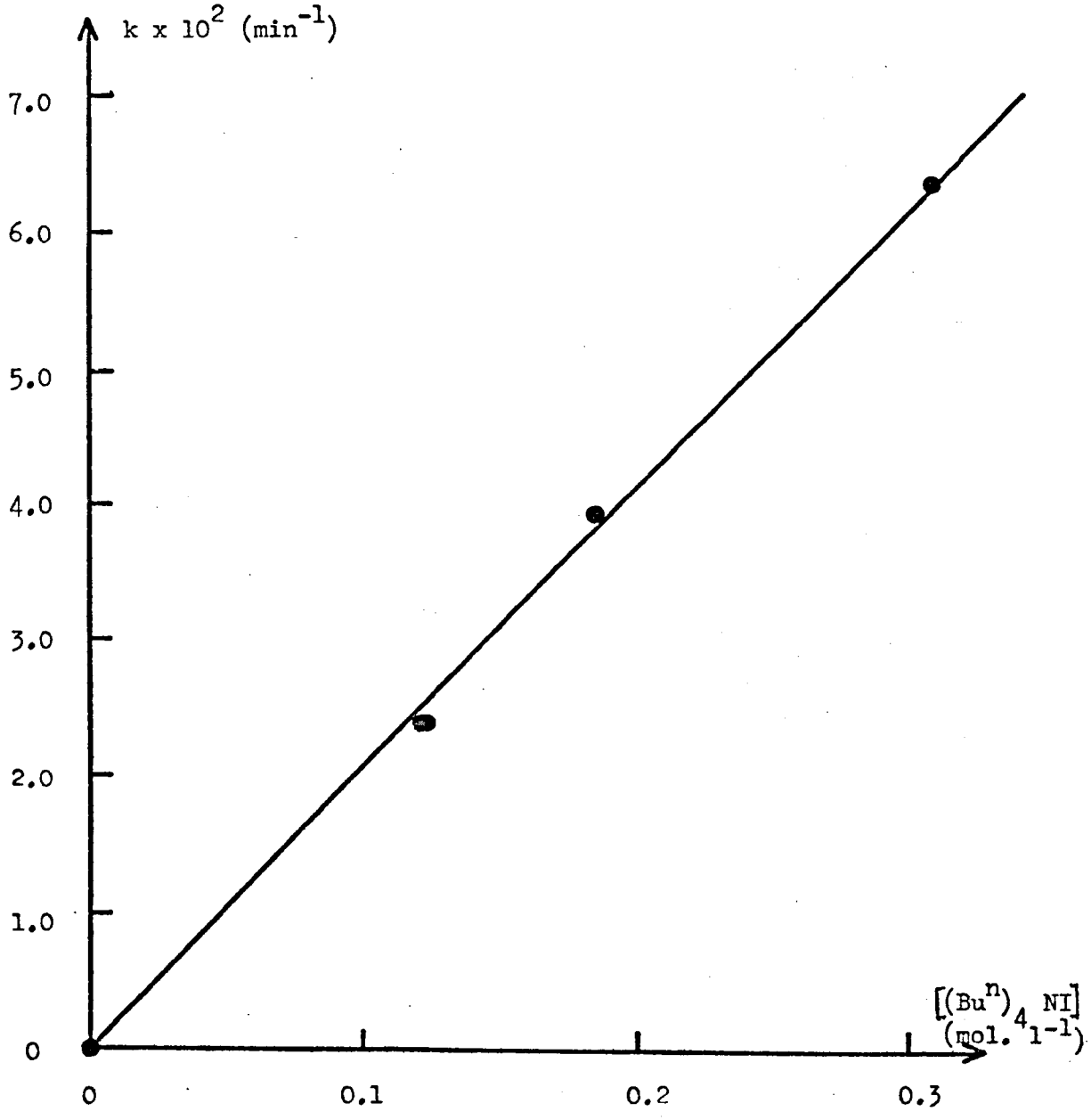

Figure 19: The variation of apparent first order rate, k for the decay of $Co_2(CO)_8$ with $[(Bu^n)_4\ NI]$

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this system offers a far better guide to effects such as change of atmosphere, change of halide, change of the countercation and to a limited extent, solvent effects than is offered by the THF system. Unfortunately, time has not permitted these investigations to be carried out as part of this work.

3) The infrared spectra of the reaction mixtures showed a strong, broad band centred at 1880 cm^{-1}, indicating that the salt $[(Bu^n)_4N][Co(CO)_4]$ is soluble in toluene. On standing, however, the intensity of this band gradually fell indicating that slow separation of the salt may have taken place.

The use of tetracarbonylcobaltate in hydrocarbon solvents was demonstrated by the reaction of iso-valeryl chloride with $Co_2(CO)_8$ in the presence of $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)][CoCl_4]$ in toluene to give an acyl cobalt tetracarbonyl intermediate which decomposed at 60°C to give 2, 6-dimethylheptan-4-one in 10 % yield.

Valence disproportionation by known anionic disproportionating agents may be extended to hydrocarbon solvents if salts of the anion can be solubilised. For example, K(dicyclohexyl-18-crown-6)OH causes valence disproportionation of $Co_2(CO)_8$ in benzene and toluene.

1.14 millimoles of $Co_2(CO)_8$ reacted with 1.64 mmole of allyl bromide in 20 ml toluene in the presence of 1.4×10^{-2} M $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]OH$ to give allyl cobalt tricarbonyl. The reaction took about three hours at room temperature.

Crown-complexed potassium salts and quaternary alkyl ammonium halides are soluble in halogenated solvents. Valence disproportionation of cobalt carbonyls may be brought about by these

solutions. These solutions do not, however, provide a useful medium for reactions involving tetracarbonylcobaltate, because of reactions between the anion and the solvent. For example, an attempt to use $Co(CO)_4^-$ in methylene chloride resulted in the production of 1, 2 dichloroethane. The reaction of tetracarbonylcobaltate (1-) with geminal dihalides has been reported[192, 193].

SECTION FOUR : EXPERIMENTAL

A: Materials and General Procedures

All work was carried out in an efficient, spark-proof fumehood.

i) reagents

Octacarbonyldicobalt was used as received from the manufacturers, without further purification. This thermally and oxidatively unstable material was stored under nitrogen or argon at -5 °C. Exposure to the atmosphere was minimised, although such operations as weighing were carried out in the air.

Dodecarbonyltetracobalt was formed by the thermal decomposition of octacarbonyldicobalt[13] in n-heptane[94].

1.239 g $Co_2(CO)_8$ was dissolved in 50 ml n-heptane under 1 atmosphere of dried, oxygen-free nitrogen in a three-necked round bottomed flask. The solution was stirred at 55 °C for twenty hours. An infrared spectrum recorded after this time showed that complete conversion to $Co_4(CO)_{12}$ had occurred. The solution was filtered under 1 atmosphere of dried, oxygen-free nitrogen in a Schlenk filter. A small amount of purple cobaltous carbonate was removed by this method.

The limb of the Schlenk apparatus which contained the solution

was cooled to -78 °C by surrounding with solid CO_2. After two hours, a mass of lustrous black crystals were filtered out at -78 °C. These crystals were washed with 100 ml of cold n-heptane. Heptane was removed by purging with nitrogen. The crystals were collected in an argon-purged three-necked flask and stored at -5 °C until required.

Anhydrous cobaltous chloride, prepared by the dehydration of hexaquocobalt(II) dichloride in thionyl chloride[194] was furnished by Dr. H.A. Brown-Acquaye.

Bis-(dicyclohexyl-18-crown-6 potassium)-tetrahalocobaltate $[K(\text{dicyclohexyl-18-crown-6})]_2[CoX_4]$. (X = Cl or Br): Hexaquacobalt(II) dihalide was dissolved with a large (~10 fold) excess of the corresponding potassium halide in water in a large crystallising dish. The water was evaporated to leave an intense blue (X = Cl) or turquoise (X = Br) solid (which turned pink on cooling). The hot solid was transferred to a large round-bottomed flask. The flask was then attached to a system capable of producing a vacuum of 0.05 torr.

The solid was flame dried and water was collected in a trap surrounded by liquid nitrogen. After about ten minutes, an oil bath was applied and the solid was left at 125 °C and 0.05 torr for 24 to 48 hours.

The vacuum was replaced by an atmosphere of dried, oxygen-free nitrogen after which a solution of dicyclohexyl-18-crown-6 in sodium-dried benzene or toluene was added.

The electronic spectrum of the blue solution of

$K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)_2CoCl_4$ thus formed is distinct from that of $[Co(dicyclohexyl\text{-}18\text{-}crown\text{-}6)][CoCl_4]$ in benzene, and shows no evidence of the presence of the hexaquocobalt (II) ion. (see section 5 this chapter).

Anhydrous lithium chloride, obtained commercially, was further dried by heating at reduced pressure (cf K_2CoX_4).

Tetra-n-butyl ammonium iodide was recrystallised from ethanol to remove all vestiges of yellow colouration.

Unless otherwise stated, all other reagents were used as received.

ii) Solvents and Gases

Ethereal solvents: The dehydration of these solvents using various drying agents is accompanied by the danger of explosion[195]. Since these explosions appear to be caused by peroxides which form fairly slowly, and are dangerous only at higher concentrations[196], it seems sensible to employ a few simple safeguards: A high turnover rate in the use of the ether means that long storage periods, during which peroxides can form, are avoided: When, following distillation, the volume of a given batch reaches a certain minimum, the remainder should be discarded (and the drying agent de-activated). In addition, in this work, ethereal solvents were always distilled and stored under an atmosphere of dried, oxygen-free nitrogen.

Ethereal solvents were dried, and distilled over sodium wire in the presence of benzophenone. The intense blue sodium benzophenone ketyl thus formed is immediately decomposed by water[197], and so this drying agent also serves as an indicator of the presence

of water.

Benzene and Toluene were dried over sodium wire.

All gases used, carbon monoxide, hydrogen and oxygen free nitrogen, were dried over self-indicating silica gel, phosphorus pentoxide and, finally, concentrated sulphuric acid before entering the reaction equipment.

iii) The equipment : General

All glassware was oven dried and assembled when hot. Joints and taps were made airtight by greasing with silicone or, in some cases, apiezon L. Once assembled, the apparatus was purged by a strong current of dried, oxygen-free nitrogen, followed where necessary, by a current of the reaction atmosphere. Additions of solid reagents, magnetic stirrer bars and so on were made against a strong countercurrent of nitrogen, or of the reaction atmosphere. Liquids were added and withdrawn by syringe through rubber septa.

iv) Infrared Spectra in the kinetic experiments.

a) Method of recording

Aliquots were removed from the reaction vessel by syringe and injected into RIIC FH-01 cells with synthetic sapphire windows. The cells were contained in RIIC VLT-2 variable temperature cell holders at 0 ^{o}C. (Times given in the tables refer to time from the commencement of the reaction until placing the FH-01 cell containing the mixture into the cooled cell holder.

Spectra were recorded on a Perkin-Elmer 577 spectrometer scanning at 200 cm^{-1} per minute below 2000 cm^{-1} and at 400 cm^{-1} per minute above 2000 cm^{-1}. Routinely, the region of the spectrum

between 2200 and 1600 cm^{-1} was recorded.

The cells were emptied, washed with ethanol followed by the reaction solvent and then dried in a stream of dried, oxygen-free nitrogen prior to reloading.

All the spectra were difference spectra; a matching FH-01 cell containing the reaction solvent was placed in the reference beam.

Generally speaking, infrared spectra for the non-kinetic experiments were recorded in the same manner, except that the cell holders were not cooled.

b) Errors in this method

Numerous sources of systematic and non-systematic errors can be envisaged in this system. Systematic errors are less important in this case since, except in one experiment, no quantitative conclusions have been derived. Non-systematic errors are more difficult to control and, in cases where the results are not well-behaved, more difficult to detect.

Since cobalt carbonyl decomposes to cobalt carbonate on storage, the purity of the carbonyl used is sure to have varied from experiment to experiment. For this reason, the value found for ε_{Cl} at $t = 0$ was taken as a more accurate representation of the amount of the carbonyl present than was the weight of the solid actually added.

The water content of the solvent, particularly of ethereal solvents, is another source of possible spurious variation from reaction to reaction. Reference experiments which were conducted in parallel with each experiment showed that in all cases the

effects of water, or other adventitious catalysts, were negligble compared with the effect of added $CoCl_2$(in THF).

The effect of carbon monoxide bubble formation, or of liquid leakage from the cell would be to reduce the apparent concentration of all the carbonyls present. Thus, in a case where the concentrations of starting material and product seemed abnormally low, one of these factors was suspected, and the values obtained treated with suspicion.

Both neutral and anionic cobalt carbonyls are sensitive to the presence of oxygen. While every attempt was made to eliminate this species, the possibility of its interference must be borne in mind. One effect of oxygen is the oxidation of tetracarbonylcobaltate to neutral cobalt carbonyl prior to final oxidation to divalent cobalt species. The formation of neutral cobalt carbonyls from tetracarbonylcobaltate is evidenced by the colouration of clear solutions of the anion on standing in air. It could be claimed that aeriel oxidation of $Co(CO)_4^-$ explains the apparent oscillatory behaviour in the disproportionation reaction were it not for the facts that the oscillation is reproducible and always occurs once only, shortly after the start of the reaction.

Despite the above-mentioned factors, reproducibility of initial concentration values was good. For example, Table 7 (pages 60 and 61) includes details of two separately made-up solutions of $Co_4(CO)_{12}$, both nominally 3.0×10^{-2} M. The values for $\varepsilon C_o l$ calculated from the spectra were respectively 0.694 and 0.695.

B: The Experiments

1) The valence disproportionation of $Co_2(CO)_8$ by amines

The reaction between $Co_2(CO)_8$ and amines in inert solvents is rapid. For example, 0.5349 g $Co_2(CO)_8$ reacted completely with 0.6 ml N-methyl-2-pyrrolidone in 20 ml toluene, under one atmosphere of nitrogen with rapid gas (CO) evolution within three minutes.

Addition of acyl halides, such as acetyl-, iso-butyryl- and benzoyl-chloride gave no infrared evidence of the formation of acyl cobalt-tetracarbonyl species. It is probable that the reaction between the tertiary amine used (N-methylmorpholine, and N, N, N′, N′ - tetramethyl ethylene diamine in addition to N-methyl-2-pyrrolidone) and the acyl halide occurred to give a quaternary acylammonium halide[198].

2) The reaction of tetracarbonylcobaltate with acyl halides in ethereal solvents

0.52 g $Co_2(CO)_8$ was deposited in the reaction vessel of apparatus similar to that illustrated in figure 20, under one atmosphere of dried, oxygen-free nitrogen. A flow chart of the gas stream is given in figure 21. About 25 ml THF was distilled into the reaction vessel. An infrared spectrum showed that after seven hours, the valence disproportionation of $Co_2(CO)_8$ was almost complete.

0.12 ml iso-butyryl chloride was added by syringe. An infrared spectrum recorded one hour later showed a weak band just above 2000 cm^{-1} indicating that, perhaps some acyl cobalt

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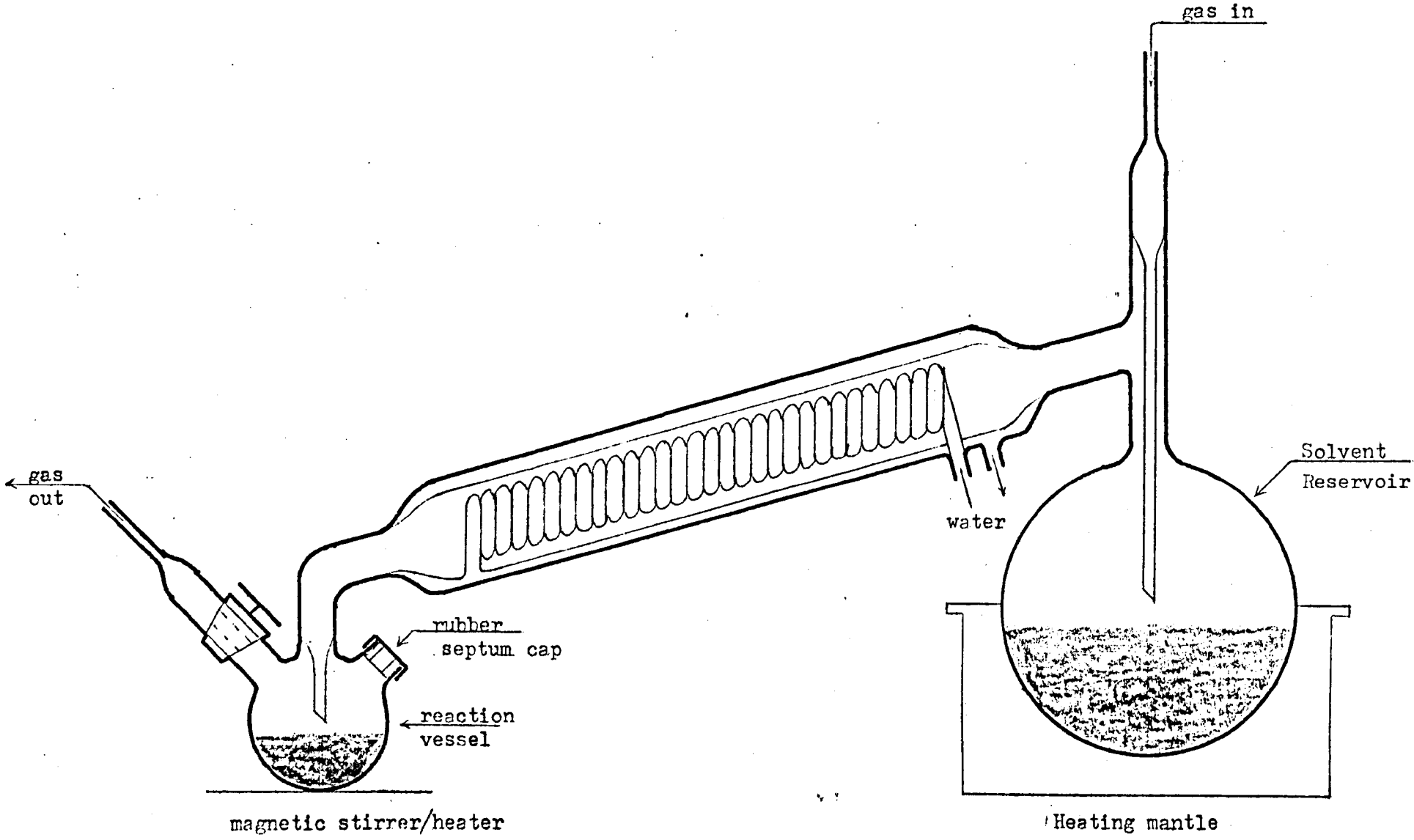

figure 20

tetracarbonyl had been formed. Another peak was evident at 1730 cm^{-1}. There was no evidence of the peak at 1810 cm^{-1} expected for iso-butyryl chloride although some tetracarbonylcobaltate remained.

An ether/water separation was performed on the evaporated reaction mixture. T.l.c. showed that one predominant product had formed. A 60 MHz n.m.r. spectrum of a solution of this product showed the following features: a) a 6-proton sharp doublet at 1.4 δ : b) a one proton septet at~2.7 δ: c) two overlapping 2-proton quintets at about 2.0 δ: d) a two proton triplet at 3.7 δ and e) a two proton triplet at 4.3 δ. This spectrum is consistent with the structure $(CH_3)_2CHCO_2(CH_2)_4Cl$. The infrared spectrum of the product is very similar to that of $(CH_3)_2CHCO_2(CH_2)_4CH_3$, the most significant difference being the presence of three strong bands at 649, 722 and 751 cm^{-1} which may be assumed to be C-Cl stretches.

The same material is formed by the reaction of $(CH_3)_2CHCOCl$ with THF in the absence of any cobalt species.

3) The formation of dodecacarbonyltetracobalt from octacarbonyldicobalt in THF

1.1736 g $Co_2(CO)_8$ was deposited in the reaction vessel of the apparatus illustrated in figure 20. About 50 ml THF was distilled into the vessel. After eighteen hours at room temperature, the contents of the vessel were examined by infrared. The spectrum was recognised as that of dodecacarbonyltetracobalt[199].

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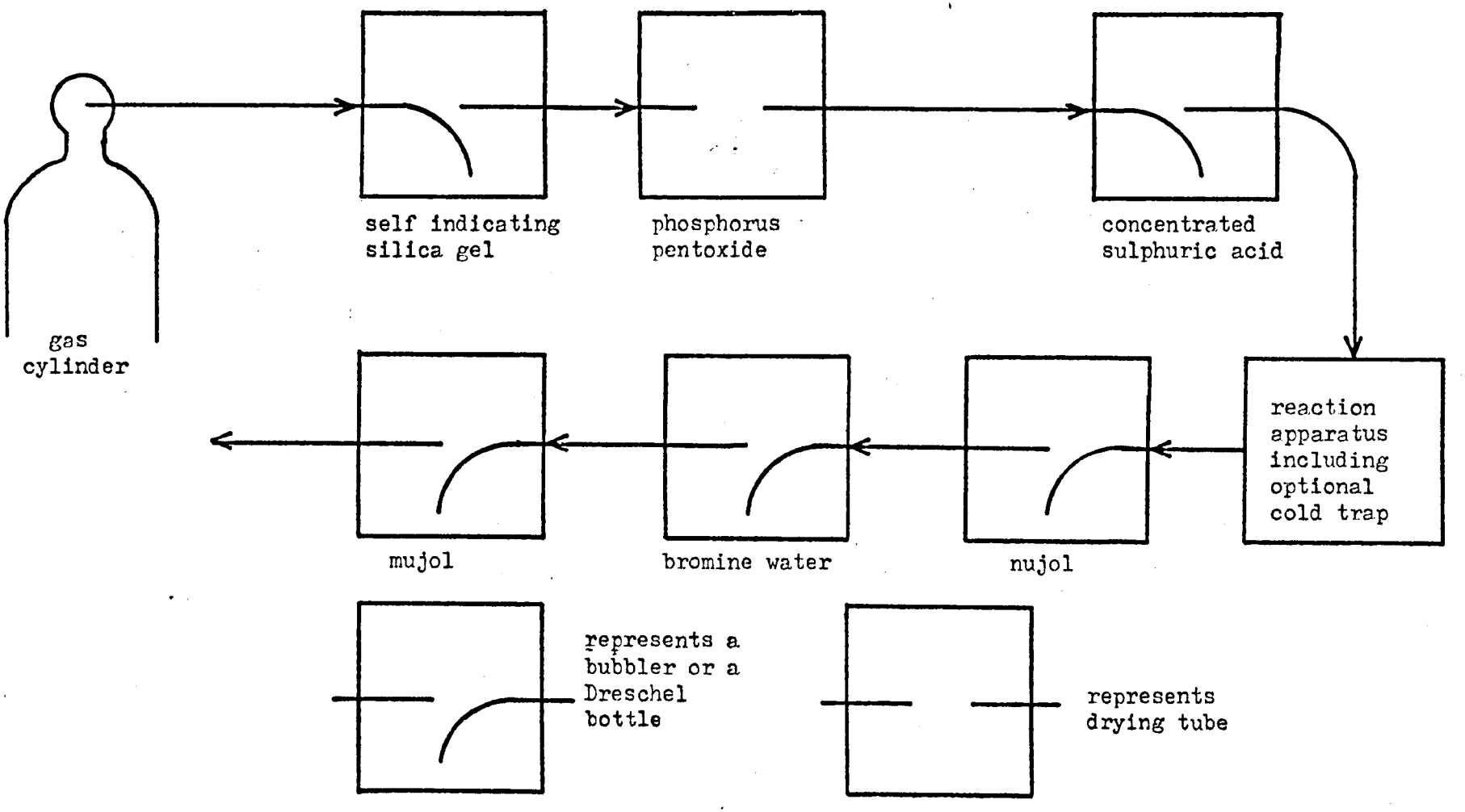


figure 21

A shoulder on the high frequency side of the bridging carbonyl band of the neutral carbonyl showed that a small degree of valence disproportionation had occurred.

4) Spectroscopic Investigation of the halide induced Valence Disproportionation of Cobalt Carbonyl in THF

Four three-necked 250 ml reaction vessels each equipped with a magnetic stirrer bar, a gas inlet, a gas outlet and a rubber septum cap were clamped in a thermostatted water bath at $25.0 \pm 0.5\ ^{o}C$.

Gas was supplied from a common source and dried as above. A manifold allowed a parallel arrangement of gas flows. The flow through individual vessels could be controlled by means of a stopcock on the gas inlet. The gas outlet led to a nujol bubbler. Each vessel was equipped with a separate bubbler. Additions of solids were made, against a nitrogen countercurrent, by removing the gas outlet.

The solutions were stirred magnetically using a 'flexi-drive' stirrer. (This is a small horseshoe magnet attached to an electric motor by means of a speedometer cable.)

As it was necessary, in these cases, to know the volume of the ethereal solvent to be used, direct distillation of the solvent was not practicable. Instead, the ether was predistilled under nitrogen and then stored for a few hours in a three necked flask under a stationary atmosphere of nitrogen at $25\ ^{o}C$.

In cases where it was desired that the cobalt carbonyl concentration should be identical for a number of reactions, three

of the flasks were charged with the requisite amount of catalyst while the other contained a known amount of $Co_2(CO)_8$ or $Co_4(CO)_{12}$.

The standard solution could then be made up by adding a known volume of the distilled THF to the vessel containing the cobalt carbonyl. After stirring for a few minutes to allow complete dissolution, the standard solution was then divided between the catalyst containing vessels. Known volumes of the cobalt carbonyl solutions were transferred by syringe. Some remaining solution was left in the original vessel to serve as a catalyst-free standard.

The reactions were carried out under a standing atmosphere of nitrogen, carbon monoxide or hydrogen. A flow of gas may have resulted in concentration of the solutions.

5) The Valence Disproportionation of $Co_4(CO)_{12}$ in the presence of water

0.0993 g $Co_4(CO)_{12}$ was dissolved in 9 ml THF, which had been distilled shortly beforehand. An i.r. spectrum was recorded. 1 ml distilled water was added. Gas evolution was immediately obvious. Infrared spectra were recorded at intervals thereafter. It was found to be impossible to achieve balancing of the infrared absorptions of the reaction solvent and reference THF-water mixtures: For this reason, no quantitative statement on the effect of added water is advanced. (Very) roughly 75 % of the dodecacarbonyl was consumed after 4.5 minutes. After 16 minutes, the i.r. showed tetracarbonylcobaltate to be the predominant metal carbonyl. A very small amount of neutral carbonyl remained.

6) The Valence Disproportionation of $Co_4(CO)_{12}$ in the presence of LiCl.

Two identical round-bottomed three-necked flasks equipped with magnetic stirrer bar, gas inlet and outlet and rubber septum cap were set up and purged with dried oxygen-free nitrogen. To one vessel was added 0.2281 g $Co_4(CO)_{12}$, and to the other, 0.2033 g $Co_4(CO)_{12}$ and 0.1912 g anhydrous lithium chloride.

Addition of 10.0 ml freshly distilled diglyme (dried as in Aii)) to the former vessel gave no immediate indication of reaction. An infrared spectrum recorded three minutes after the addition showed the spectrum of $Co_4(CO)_{12}$ with a very small absorption at 1880 cm^{-1}.

Addition of 10.0 ml freshly distilled diglyme to the other vessel gave rise to an immediate colour change from brown-black through blue-green to translucent blue. An infrared spectrum recorded two minutes thirty seconds after the addition showed an intense band at 1884 cm^{-1}, and no evidence whatsoever of $Co_4(CO)_{12}$.

7) The valence disproportionation of $Co_2(CO)_8$ by $(Bu^n)_4NI$

Four individual test tubes, equipped with quickfit stoppers were thoroughly purged with nitrogen and stoppered.

52.7 mg $(Bu^n)_4NI$ was added to tube 1, 48.0 mg $(Bu^n)_4NI$ was added to tube 3.

A solution containing 0.1097 g $Co_2(CO)_8$ was made up in 10.0 ml freshly distilled THF. After the $Co_2(CO)_8$ had dissolved, 4.0 ml of the solution was transferred to each of tubes one and two.

Another solution, containing 0.1090 g $Co_2(CO)_8$ in 10.0 ml sodium-dried benzene was made up. After dissolution, 40 ml of the solution was placed in each of tubes 3 and 4.

Furious gas evolution was noted on the addition of the solution to vessel 1. The colour of the solution had changed to green within 15 minutes and to blue within thirty. An infrared spectrum recorded 35 minutes after the addition showed that no $Co_2(CO)_8$ remained. $Co(CO)_4^-$ was the only cobalt carbonyl species present.

After 50 minutes at room temperature, the contents of vessel 2 still bore the familiar dark brown colour of $Co_2(CO)_8$ solutions. An infrared spectrum showed that only a small fraction of the neutral carbonyl had been converted to $Co(CO)_4^-$.

Bubble formation was also evident in tube 3, although this was not so spectacular as in vessel 1. A slow colour change to a cloudy brown-green took place together with deposition of a green-blue sludge. An infrared spectrum recorded 45 minutes after the addition showed a substantial quantity of $Co(CO)_4^-$ had been formed, although some $Co_2(CO)_8$ remained. An i.r of the contents of tube 4 recorded one hour after the addition was the spectrum of $Co_2(CO)_8$.

8) Valence Disportionation of cobalt carbonyls via crown complexed dipotassium tetrahalocobaltate in hydrocarbon solvents

0.804 g (1.57 x 3/2 mmole) $Co_2(CO)_8$ was dissolved in 40.0 ml of sodium-dried benzene, and an infrared spectrum recorded. 10.0 ml of a benzene solution 27.5 millimolar in $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2[CoBr_4]$ was injected. An infrared spectrum was recorded one day later. The intensity of the

2040 cm^{-1} band of $Co_2(CO)_8$ in each spectrum was compared (Table 10)

Table 10

t(hr)	I_o	I_{2040}	εcl
0	87.5	19.9	0.643
23.5	91.9	26.9	0.534

This indicates that over 23.5 hours, 17.0 % of the initial $Co_2(CO)_8$ was consumed.

9) <u>The effect of $(Bu^n)_4NI$ on hydrocarbon solutions of $Co_2(CO)_8$</u>

About 80 ml of sodium dried toluene was refluxed for four hours under a slow but steady stream of dried oxygen free nitrogen. The vessel was flushed with dried carbon monoxide and refluxing was continued for a further two hours in a slow current of CO.

The toluene was allowed to cool before being placed in a thermostatted water bath at 25.0 $\pm$ 0.5 ^oC under a stationary atmosphere of carbon monoxide.

Four one hundred ml round-bottomed, three necked flasks were set up as described in 4) above. The vessels were purged with nitrogen and then with carbon monoxide. Tetra-n-butyl ammonium iodide was added to each of the vessels as follows: 1) 0.4546 g, 2) 0.8879 g, 3) 1.3615 g, 4) 2.2586 g.

0.15 g $Co_2(CO)_8$ was added to the toluene reservoir. The solution was stirred for 30 minutes at 25.0 ^oC and infrared spectrum(OA) was recorded. 10.0 ml of the $Co_2(CO)_8$ stock solution

was added to vessel one, and 20.0 ml to each of the other vessels. I.r. spectra were recorded as in A iv). Another infrared spectrum of the stock solution was recorded after 220 minutes.

The solutions became colourless as the reaction proceeded and a green-blue powder was deposited.

10) <u>The effect of [Co(dicyclohexyl-18-crown-6)][$CoCl_4$] on hydrocarbon solutions of cobalt carbonyl</u>

5 g anhydrous cobaltous chloride and 2.8998 g dicyclohexyl-18-crown-6 were shaken thoroughly in 25.0 ml of sodium dried toluene (which had previously been refluxed under nitrogen and CO as in 9) above) under one atmosphere of carbon monoxide. The blue colour which appeared in solution was taken as evidence for the formation and dissolution of (dicyclohexyl-18-crown-6)cobalt(II) tetrachlorocobaltate(II). The electronic spectrum of the solution was recorded. This is described in section 5.

1.1222 g $Co_2(CO)_8$ was added to 50.0 ml of similarly treated toluene under one atmosphere of carbon monoxide at 25.0 °C.

Four 100 ml round bottomed flasks were set up as in 4) above and purged with CO. 10.0 ml [(Co(dicyclohexyl-18-crown-6)][$CoCl_4$] solution was placed in vessel 1), 5.0 ml in vessel 2, 3.0 ml in vessel 3) and 2.0 ml in vessel 4). The contents of each vessel were then made up to 10.0 ml by adding the requisite amount of the refluxed toluene.

10.0 ml $Co_2(CO)_8$ solution was added to each of the four reaction vessels. The reactions were monitored on infrared as in A iv) above. The reactions proved to be extremely slow. More than

90 % of the starting $Co_2(CO)_8$ remained in vessel 1) after 24 hours. A small shoulder at 1880 cm^{-1} showed that some anion had been formed and was maintained in solution.

11) The formation of 2,6-dimethylheptan-4-one from iso-valeryl chloride in hydrocarbon solvents

0.6686 g $Co_2(CO)_8$ and 0.3 ml iso-valeryl chloride were added to 30 ml of benzene approximately 2 x 10^{-3} molar in $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)][CoCl_4]$ under 1 atmosphere of N_2. The reaction mixture was allowed to stir at room temperature overnight. An infrared spectrum showed mainly $Co_2(CO)_8$, but with definite distortions at 2005 cm^{-1} and at 2023 cm^{-1}, and there is a weak, sharp band at 2105 cm^{-1}. Heating the solution to 60 °C for about five hours brought about disappearance of all of the metal carbonyl bands in the infrared spectrum. A broad, untidy peak was present in the region of 1700 cm^{-1}. A t.l.c. of the mixture (toluene eluent on silica stationary phase) showed a faint spot at R_f 0.55 on spraying with 2,4-dinitrophenylhydrazine (d.n.p.) solution.

A few grams of silica were added to the reaction mixture and the solvent evaporated at reduced pressure. The reaction mixture-adsorbed silica was placed atop a silica column of diameter 2 cm. The dead volume of the column was almost exactly 100 ml. The column was eluted with toluene. 5 ml fractions were collected and tested by analytical t.l.c. The fractions of standard eluted volume between 2.30 and 2.90 showed a weak d.n.p. positive spot corresponding to that in the reaction mixture. Evaporation of these combined fractions revealed a small amount of brown sludge. Extraction of this material with a solution of 2,4-dinitrophenyl-hydrazine in ethanol and hydrochloric acid gave a golden yellow

powder, which on recrystallisation from ethanol gave a yellow powder melting at 92 - 93 °C (lit. 93 - 94 °C for the 2,4-dinitrophenylydrazone of isovalerone[200]). 0.0701 g of the hydrazone was collected indicating a final yield of 9 %.

12) The formation of allyl cobalt tricarbonyl from $Co_2(CO)_8$ and allyl bromide in toluene in the presence of K(dicyclohexyl-18-crown-6)OH

A 100 ml round-bottomed, three necked flask was equipped with a magnetic stirrer bar, a gas inlet, a gas outlet and a rubber septum cap. The vessel was purged with dried, oxygen-free nitrogen.

0.3889 g $Co_2(CO)_8$ was dissolved in 20.0 ml sodium-dried toluene in the vessel. There was no sign of valence disproportionation over 23 hours at room temperature.

0.14 ml of freshly distilled allyl bromide was added to the vessel. Twenty minutes later, a small amount of green solid had formed on the vessel wall. An infrared spectrum recorded at this time indicated that a small amount of allyl cobalt tricarbonyl had formed.

30 minutes after the addition of the allyl halide, 1.8 ml of a toluene solution 0.17 M in K(dicyclohexyl-18-crown-6)OH was added. An infrared spectrum recorded seven minutes later shows a dramatic increase in the concentration of allyl cobalt tricarbonyl. There is also some evidence of the presence of $Co(CO)_4^-$. The reaction mixture gradually became cloudy and purple-pink. After three hours at room temperature, the bridging band of $Co_2(CO)_8$ was barely visible on i.r. The dominant features in the spectrum were

a strong sharp band at 2064 cm^{-1} and a very strong band at 1989 cm^{-1}. (lit.[201] 2066 cm^{-1} (m) and 1984 cm^{-1} (s)).

0.8 ml triphenyl phosphite was added to the mixture .

Three hours later, an infrared spectrum showed two predominant bands at 2018 cm^{-1} (strong and sharp) and at 1958 cm^{-1} (strong). (lit.[202] 2019, 1974 and 1984 cm^{-1} in cyclohexane). No attempt was made to isolate the product.

13) Valence disproportionation of cobalt carbonyl in methylene chloride

Two identical round-bottomed, three-necked flasks were equipped with a gas inlet, gas outlet, rubber septum cap and a magnetic stirrer bar. The vessels were purged with dried, oxygen-free nitrogen.

To one vessel was added 0.1007 g (0.29 mmole) $Co_2(CO)_8$, 0.8450 g K_2CoCl_4 and 0.0659 g (0.18 mmole) dicyclohexyl-18-crown-6. 0.1078 g $Co_2(CO)_8$ was deposited in the other vessel. 20 ml dried (4A molecular seives) CH_2Cl_2 was syringed into each vessel.

No signs of valence disproportionation were evident after 46 hours in the absence of $[K(\text{dicyclohexyl-18-crown-6})][CoCl_4]$.

An infrared spectrum of the solution containing $[K(\text{dicyclohexyl-18-crown-6})][CoCl_4]$ was recorded 7 minutes after addition of the solvent. In this case, the 1880 cm^{-1} band due to $Co(CO)_4^-$ was already more intense than the bridging carbonyl band of $Co_2(CO)_8$. In this vessel, the concentration of $Co(CO)_4^-$ continued to rise to a maximum attained after about 7 hours. 24 hours later, no further increase in the $Co(CO)_4^-$ concentration

could be detected, despite the fact that a substantial amount of $Co_2(CO)_8$ remained. This is consistent with the formation of the soluble salt [K(dicyclohexyl-18-crown-6)] $[Co(CO)_4]$ (vide supra).

A water condenser was inserted between the reaction vessel and its nitrogen outlet. The solution containing partially disproportionated $Co_2(CO)_8$ was refluxed for 18 hours under one atmosphere of nitrogen. After this time, an infrared spectrum showed only an indistinct area of absorption above 2000 cm^{-1}. (A fairly intense peak was present at 1720 cm^{-1}, but the species responsible for this was not identified).

Water was added to the mixture and a water/methylene chloride separation performed. The organic layers were dried over $MgSO_4$, filtered and carefully evaporated. A small amount of liquid remained. T.l.c. showed this to be essentially one compound, with one very minor impurity.

60 MHz n.m.r. of this liquid in $CDCl_3$ showed an intense singlet at 3.71 δ, superimposable with the spectrum of 1,2-dichloroethane. A very much weaker multiplet was to be seen at about 4.3δ.

14) Hydridotetracarbonylcobalt(I) and its detection

Although $HCo(CO)_4$, when formed, was often detected by infrared in reaction mixtures, a downstream cold-trap at -78 °C was employed when the presence of this volatile species was suspected. Usually, sufficient solvent would also be trapped to allow recording of a normal solution spectrum. $HCo(CO)_4$ certainly seems to survive for long enough at 0 °C to allow its spectrum to be recorded.

Allowing a cold trap containing the hydrocarbonyl to warm to

room temperature caused the appearance of a yellow colour, indicating that at least some of the $HCo(CO)_4$ had decayed to $Co_2(CO)_8$. Volatilised $HCo(CO)_4$ was allowed to pass through a nujol bubbler before being oxidised in a bromine water bubbler. The nujol bubbler was employed to prevent back diffusion of water and bromine to the reaction vessel.

$HCo(CO)_4$ was detected in solution and in the cold trap when aqueous HCl was added to a solution containing $Co_2(CO)_8$ or $Co_4(CO)_{12}$, and also when acyl halides were added to cobalt carbonyl solutions. No $HCo(CO)_4$ was detected by this method during valence disproportionation of $Co_4(CO)_{12}$ under one atmosphere of hydrogen.

SECTION FIVE : THE ELECTRONIC SPECTRA OF COBALT HALIDES IN ORGANIC SOLVENTS

All spectra were recorded on a Unicam SP800B spectrometer.

The spectra of $[K(\text{dicyclohexyl-18-crown-6})]_2[CoX_4]$ in benzene show great similarities to the reported spectra of the corresponding tetrahalocobaltate salts in media of low polarity.

Table 11 summarieses these similarities.

Table 11

$[(Bu^n)_4N]_2CoCl_4$ + Xs $(Bu^n)_4NCl$ in CH_2Cl_2 [189]	$K(\text{crown})CoCl_4$ in benzene	$(QH)_2Co\,Br_4$* in HCBD [188]	$K(\text{Crown})\,CoBr_4$ in benzene
531 (0.013)	531(0.01 to 0.02)	620 (0.138)	620 (sh)
617 (sh)	615 (sh)	641 (0.370)	642 (0.46)
635 (0.613)	632 (0.60)	668 (0.651)	672 (sh)
669 (0.844)	670 (0.93)**	705 (1.000)	706 (1.00)
699 (1.000)	692 (1.00)	730 (0.927)	750 (sh)

Wavelengths in nanometres, figures in parentheses are intensities relative to the most intense peak. *QH represents the quinolinium ion. ** This value was reproducible.

No trace of $Co(H_2O)_6^{2+}$ was detected in these spectra.

The spectrum of anhydrous $CoCl_2$ in THF shows certain differences from that of $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)][CoCl_4]$ in benzene. The most significant of these deviations is the presence of a band at 593 nm. The intensity of this band is about 0.56 times that of the most intense band in the spectrum. This most intense band arises at 685 nm and has shoulders at 670 and 630 nm.

This can be interpreted as the spectrum of $[Co(THF)_6][CoCl_4]$ where the absorption at 593 nm is due to the THF complexed Co^{II}, while the other absorptions arise from the anion.

The general envelope shape of the spectrum of $[Co(dicyclohexyl\text{-}18\text{-}crown\text{-}6)][CoCl_4]$ in benzene closely resembles the spectrum of $CoCl_2$ in THF. The band due to the crown ether complexed Co^{II} is less well-resolved from the anion bands, and is observed as a shoulder at about 600 nm. Intensity relative to ε_{max} is 0.59. λ_{max} is at 680 nm, with shoulders at 645 nm and 625 nm. It is tentatively suggested that tighter ion pairing in the less polar solvent and with the divalent cation could alter the symmetry of the system and thereby substantially affect the spin-orbit coupling responsible for the fine structure of the observed band. The apparent high intensity of the octahedral divalent cobalt species could be misleading, since it is possible that some $[Co(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]Cl_2$ exists in these solutions.

CHAPTER THREE

THE FORMATION AND THERMAL DECOMPOSITION OF ALKYL COBALT TETRACARBONYL SPECIES

CHAPTER THREE : THE FORMATION AND THERMAL DECOMPOSITION OF ALKYL COBALT TETRACARBONYL SPECIES

SECTION ONE : INTRODUCTION

The reactions between tetracarbonylcobaltate(1-) and the generalised alkyl halide, RX, and acyl halide, RCOX lead respectively to the generation of alkyltetracarbonylcobalt(I), $RCo(CO)_4$ [203] and the acyltetracarbonylcobalt(I), $RCOCo(CO)_4$ [183].

$RCo(CO)_4$ and $RCOCo(CO)_4$ are interconvertible [39] according to the equilibrium , (34).

$$RCo(CO)_4 + CO \rightleftharpoons RCOCo(CO)_4 \qquad (34)$$

The intermediates are susceptible to a number of re-arrangements which depend on the precise nature of R as well as on the conditions. All of these arrangements appear to depend on the intermediacy of a co-ordinately unsaturated, 16-electron cobalt species, formed in one of the equilibria (35) or (8):

$$RCo(CO)_4 \rightleftharpoons RCo(CO)_3 + CO \qquad (35a)$$

$$RCOCo(CO)_4 \rightleftharpoons RCOCo(CO)_3 + CO \qquad (35b)$$

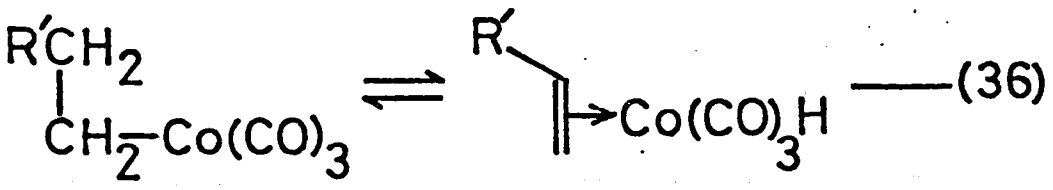
$$RCo(CO)_4 \rightleftharpoons RCOCo(CO)_3 \qquad (8)$$

No evidence is available on the precise mechanism of process (8), but there is no reason to suspect that this should be substantially different from the alkyl migration mechanism for the interconversion of alkyl- and acyl- manganese carbonyls [204].

Subsequent complexation by a suitable two electron ligand may occur intermoleculary or intramoleculary. Both alkyl- and acyl-cobalt tetracarbonyl react with triphenylphosphine to give the acyl cobalt tricarbonyltriphenylphosphine adduct [205]. Where a

potential two electron ligand exists in R 5 or 6 atoms distant from cobalt, a metallacycle may be formed. For example, carboethoxyacetylcobalt tricarbonyl exists with one of the ester oxygens co-ordinated to cobalt[183]. Where R is an allyl group, the trihapto-allyl cobalt tricarbonyl may be formed[190, 201, 206].

The β-elimination mode of decomposition of alkyl cobalt tetracarbonyl[164] may reasonably be compared to the above processes:



—(36)

In (36), the incoming 2-electron donor is the olefin group. H replaces R as the one-electron ligand. The β-elimination process is reversible, and can give rise to isomerisation of the alkyl cobalt intermediate[207].

The above rearrangements often occur prior to the thermal or chemical decomposition of alkyl- or acyl- cobalt tetracarbonyls and can have considerable effect on the nature of the resultant products.

The thermal decomposition of alkyl cobalt tetracarbonyls to give dialkyl ketones has been described (chapter one).

Thermal decomposition of alkyl cobalt tetracarbonyls by alkyl carbon-cobalt bond homolysis has been noted in some cases where the alkyl fragment bears a halogen or an aromatic group on the α-carbon.[193]

SECTION TWO : THE REACTIONS OF HALOMETHYL- AND O-BIS-HALOMETHYL-ARENES WITH TETRACARBONYLCOBALTATE(1-)

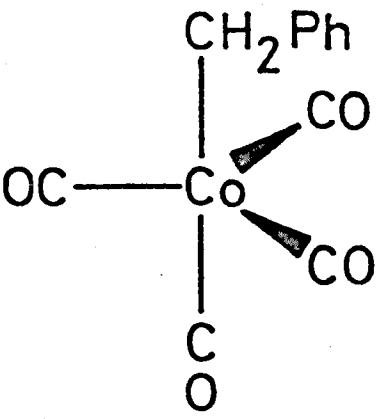
Inspection of an infrared spectrum of the products of the reaction between benzyl bromide and tetracarbonylcobaltate in THF under an atmosphere of nitrogen at ambient temperature showed a band of medium intensity at 2102 cm^{-1} with a definite shoulder at 2112 cm^{-1}. A strong band at 2014 cm^{-1} showed slight broadening at about 2030 cm^{-1} and a shoulder at 2058 cm^{-1}.

The application of one atmosphere of CO brought about an increase in intensity in the band at 2112 cm^{-1}. The band at 2102 cm^{-1} was reduced in intensity and appeared as a shoulder of the former band. The band at 2014 cm^{-1} remained the dominant feature in the spectrum, and the shoulder at 2058 cm^{-1} was still present. A definite shoulder had emerged at 2030 cm^{-1}, and another significant shoulder was present at 2005 cm^{-1}. An area of absorption had emerged at 1735 cm^{-1}.

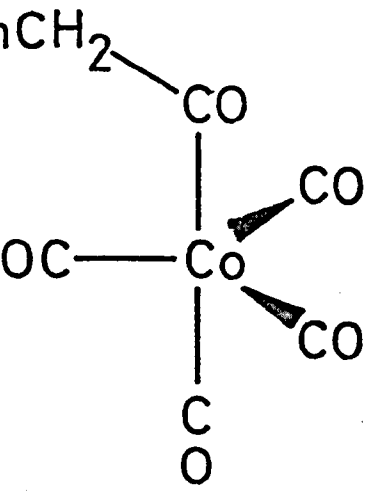
These observations can be interpreted in terms of a shift in the equilibrium, (37)

$$PhCH_2\,Co(CO)_4 + CO \rightleftharpoons PhCH_2COCo(CO)_4 \qquad (37)$$

The bands at 2102 cm^{-1}, 2058 cm^{-1} and 2014 cm^{-1} are assigned respectively to the a_1 (equatorial), a_1 (axial) and e (equatorial) stretches of the alkyl cobalt tetracarbonyl(XIV)[cf 63a,208].



(XIV)



(XV)

The band at 2112 cm^{-1} is assigned to the totally symmetric stretch of the equatorial carbonyl groups of phenylacetyl cobalt tetracarbonyl (XV). The e band is split into two absorptions at 2005 cm^{-1} and 2030 cm^{-1}, presumably because of the influence of the phenylacetyl group (cf $PhCH_2CO\text{-}Co(CO)_3PPh_3$[209]). The absorption at 1735 cm^{-1} is due to the phenylacetyl carbonyl stretch. The expected band arising from the stretch of the axial carbonyl group has presumably been masked by the 2058 cm^{-1} band of benzyl cobalt tetracarbonyl.

Increasing the temperature to 60°C over 2 hours caused reversion to the alkyl species. Continued heating caused destruction of the alkyl cobalt intermediate. Dibenzyl ketone (1,3-diphenylpropan-2-one) was formed in 45 % yield. Toluene and, in some cases, 1,2-diphenylethane were detected in the product mixtures.

Benzyl cobalt tetracarbonyl may be formed in benzene by the reaction of benzyl bromide with $Co_2(CO)_8$ in the presence of soluble

disproportionating agents. Infrared absorptions are observed at 2100 cm^{-1}, 2055 cm^{-1} (sh) and 2010 cm^{-1}. Thermal decomposition of the intermediate at 50 °C under one atmosphere CO in benzene gives dibenzyl ketone in yields of up to 69 %. 1,2-diphenylethane (25 %), diphenylmethane (11 %) and toluene (detected) are also formed.

It is difficult to envisage a mechanism which accounts for the formation of diphenylmethane in benzene, but not in tetrahydrofuran which does not involve benzyl radicals: Homolytic scission of the cobalt carbon bond is indicated[cf 193].

It seems likely that 1,2-diphenylethane is formed by the combination of two benzyl radicals. Toluene may arise by hydrogen atom abstraction by the benzyl radical from THF or from benzene. Diphenylmethane is formed by homolytic substitution of a benzyl radical on benzene.

The fact that the product of cobalt-carbon bond homolysis in this case is the frequently encountered benzyl radical may indicate that Co-C scission is governed by the same effects involved in, for example, carbon-halogen bond scission. There is no evidence in the literature and none has been found during this work, to suggest that coupling of alkyl halides by $Co(CO)_4^-$ occurs except where the alkyl radical is stabilised, for example, by delocalisation.

In benzene, the predominant by-product is 1,2-diphenylethane, whereas in THF, toluene is formed to a greater extent. The relative yields of these two products will, of course, depend on the concentration of radicals present, but in this case, a greater

tendency for THF to undergo hydrogen abstraction may be indicated. The fact that diphenylmethane is formed in benzene illustrates the preference of aromatic species to suffer homolytic substitution rather than hydrogen abstraction[210].

The reason for the greater yield of carbonylated product is not clear: Carbon monoxide is less soluble in benzene than in ethers[211]. There is evidence in the literature that good co-ordinating solvents, such as THF, aid reactions in which (apparently) co-ordinately unsaturated metal intermediates are involved[e.g.212]. The equilibrium, (38), should be driven to the right where So is a good co-ordinating solvent, but then so should equilibrium (39)[cf 212].

$$RCo(CO)_4 + So \rightleftharpoons RCo(CO)_3(So) + CO \quad \text{——— (38)}$$

$$RCo(CO)_4 + So \rightleftharpoons RCOCo(CO)_3(So) \quad \text{——— (39)}$$

R = alkyl, So = solvent

It was found that freshly distilled benzyl bromide failed to react with octacarbonyldicobalt at room temperature in the absence of a disproportionating agent. Seyferth[193] has observed that the reaction does take place under similar conditions at higher temperatures.

Heating colourless benzyl bromide with octacarbonyldicobalt in refluxing benzene in the complete absence of added disproportionating agents was found to give rise to benzyltetracarbonylcobalt(I): Infrared absorptions were present at 2102 cm^{-1} and at 2012 cm^{-1}. A strong, sharp band at 2052 cm^{-1} and a strong, broader band at 1985 cm^{-1} may indicate the presence of (η^3 - benzyl)-tricarbonylcobalt(I).

Continued heating destroys the organocobalt intermediates and yields dibenzyl ketone (54 %), 1,2-diphenylethane (25 %) and diphenylmethane (11 %) based on reacted benzyl bromide.

Filtration of the reaction mixture revealed a green-blue solid which was assumed to be cobaltous bromide, and a yellow-green solution. The electronic spectrum of this solution shows an envelope from about 520 nm to about 720 nm. Maxima occur at 600, 624, 658 (λ_{max}) and at about 680 nm (sh). The spectrum could not be mistaken for that of the tetrabromocobaltate (2-) ion in benzene, but the position of the band and its complex structure infer the presence of an approximately tetrahedral divalent cobalt species.

In none of the reactions involving benzyltetracarbonylcobalt(I) was evidence for the formation of o-tolyltetracarbonylcobalt(I) found[213]. The presence of carbon monoxide, and absence of a potential source of hydridotetracarbonylcobalt(I) no doubt hindered this mode of isomerisation.

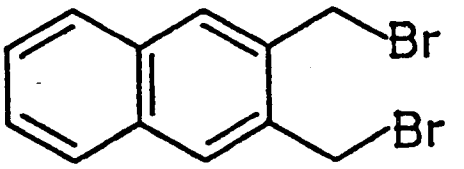
The reaction between dibromo-o-xylene and octacarbonyldicobalt in benzene in the presence of $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2\ [CoBr_4]$ at 60 °C gives an alkyl cobalt tetracarbonyl species. This intermediate was not isolated, but was recognised by infrared absorptions at 2105 cm^{-1} amd at 2010 cm^{-1}. (The a_1 (axial) band was presumably masked by the absorptions of some dodecacarbonyltetracobalt which was present). A weak absorption was also noted in the i.r. at 1755 cm^{-1}.

Continued heating destroyed the organocobalt intermediate to

give 2-indanone in good yield. (Yields of up to 80 % have subsequently been achieved by varying the temperature of the initial reaction and of the thermal decomposition[214]).

The fact that yields obtained in this reaction appear to be slightly higher than in the formation of dibenzyl ketone from benzyl bromide may indicate that the ortho-dimethyl arene system functions as a template, bringing the two reactive 'ends' of the molecule together.

The infrared spectrum of the product of the reaction of two moles of tetracarbonylcobaltate(1-) with 2,3-bis-(bromomethyl)-naphthalene (XVI) shows a strong, sharp peak at 2047 cm^{-1} and a very strong band at 1991 cm^{-1}.



(XVI)

This spectrum is inconsistent with the formation of a tetracarbonyl species analogous in structure to benzyl cobalt tetracarbonyl. The spectrum is reminiscent of that of (η^3-allyl) cobalt tricarbonyl: The high frequency band being the i.r. allowed totally symmetric carbonyl stretch, the lower arising from the degenerate out-of-phase modes.

The intermediate reacts with triphenylphosphine to yield a species giving rise to a strong infrared absorption at 1970 cm^{-1} and at 1914 cm^{-1}. This spectrum is analogous to that of (η^3-allyl)dicarbonyl(triphenylphosphine)cobalt(I).

Reaction of the tricarbonyl intermediate in benzene with triphenylphosphite gives a species with a similar spectrum. Both carbonyl frequencies are perceptibly split in this case, however. A strong, sharp band at 2010 cm^{-1} bears a distinct shoulder at 2000 cm^{-1}. The lower frequency band in the spectrum has two maxima, one at 1959 cm^{-1} (slightly more intense), the other at 1970 cm^{-1}.

Trimethylphosphite reacts similarly to give a species with i.r. absorptions at 2000 cm^{-1}, 1989 cm^{-1} (shoulder, about half as intense as the main band) and at 1940 cm^{-1}. No splitting is detected in this broad band.

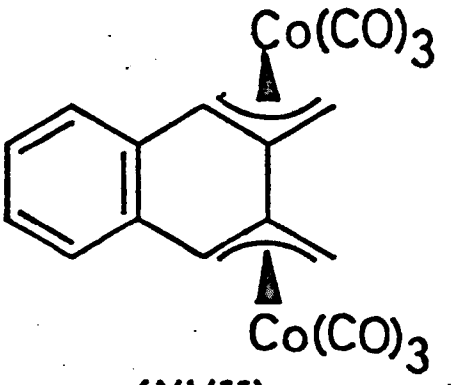
These observations are consistent with the existence of rotational isomers arising from restricted rotation about the P-O-C system in the ligands[215]. This has been observed for other $(\eta^3\text{-allyl})Co(CO)_2P(OR)_3$ systems [202].

It should be noted that the failure to observe splitting in the spectrum of the triphenylphosphine derivative may be due to the smaller degree of splitting in this case[cf 202]. On the other hand, any splitting may be masked by solvent induced broadening: This spectrum was recorded in THF, while those of the $P(OMe)_3$ and $P(OPh)_3$ derivatives were recorded in benzene.

The stoichiometry of the reaction of 2,3-bis-(bromomethyl)-naphthalene with tetracarbonylcobaltate and the stoichiometries of the reactions of the intermediate thus formed with phosphine and phosphites indicate that both bromine atoms are substituted.

The spectra of the bis-tricarbonyl and of its phosphine and

phosphite derivatives are directly analogous to those for η^3-allyl cobalt tricarbonyl and its derivatives. No evidence of a significant metal-metal liaison is indicated[216]. The structure, (XVII) is proposed for the intermediate.



(XVII)

This intermediate decomposed at 60 °C under one atmosphere of CO in THF to give 1,3-dihydro-(2H)-benz-[f]-inden-2-one in 40 % yield. The only observed by-product of the decomposition was 2,3-dimethylnaphthalene.

In benzene solution, thermal decomposition of (XVII) leads to the formation of 1,3-dihydro-(2H)-benz-[f]-inden-2-one in 55 % yield. 1,2-Dihydrocyclobuta-[b]-naphthalene was identified as a major by-product, accounting for up to 25 % of the starting 2,3-bis-(bromomethyl)-naphthalene. 2,3-dimethylnaphthalene was also formed in this reaction.

Again, the by-products of the thermal decomposition of this benzyl cobalt carbonyl analogue indicate that homolysis of the cobalt-carbon bond has occurred. Again, the yield of carbonylated product is higher in benzene than in THF.

2,3-Bis-(bromomethyl)-quinoxaline reacts with tetracarbonylcobaltate, but again, the product of the reaction is

not a simple alkyl cobalt tetracarbonyl. Infrared absorptions are observed at 2050, 1994 and 1961 cm^{-1}, and a comparatively weak band is present at 1691 cm^{-1}. The spectrum is illustrated in figure 22

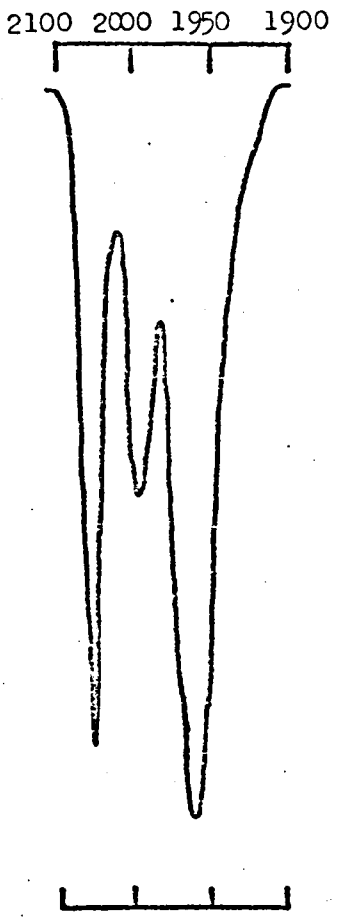
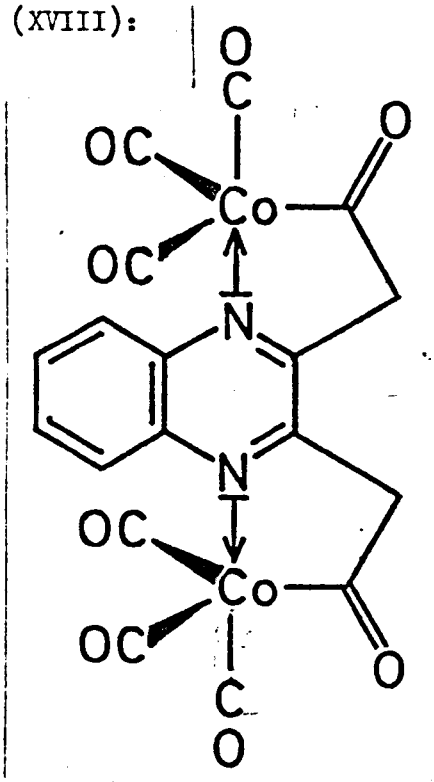


figure 22: The terminal carbonyl stretching region of the infrared spectrum of the product of the reaction between tetracarbonylcobaltate and 2,3-bis-(bromomethyl)-quinoxaline.

The spectrum can be explained as that of a species of the type (XVIII):



(XVIII)

Only local stereochemistry about each cobalt centre is indicated in this diagram: There is no intention to imply total molecular conformation.

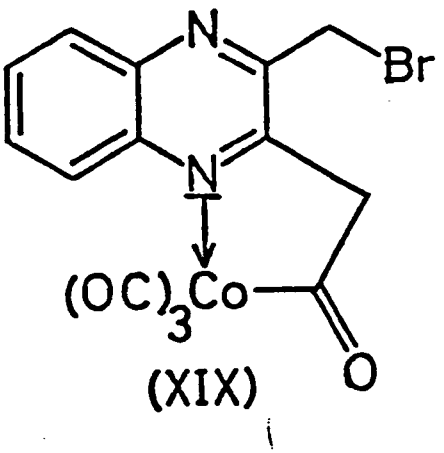
The a_1 (ax), a (eq) and b (eq) modes of carbonyl vibration for such a system are all expected to be i.r. allowed.

The species (XVIII) is analogous to the series of compounds discovered by King[217] following the reactions between pentacarbonylmanganate(1-), and some other metal carbonyl anions, with various haloalkylamines, including 2-(bromomethyl)-pyridine.

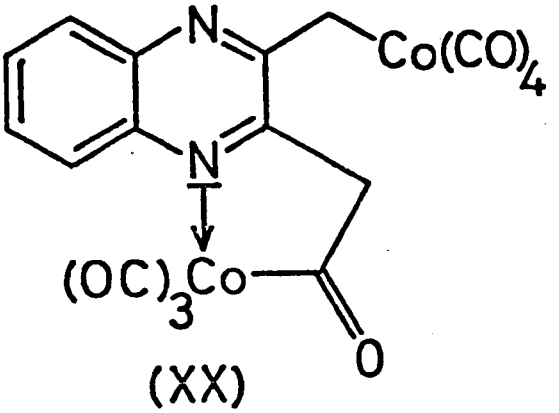
The ready formation of this intermediate is, perhaps, slightly surprising considering the low basicity of quinoxaline compared with pyridine[218]. Poor σ-donicity may, however, be countered by some π-acceptance by the aromatic system[217]. 2,3-Dimethylquinoxaline shows a marked reluctance to undergo quaternisation of both nitrogen atoms[219] although quaternisation of both nitrogen atoms of quinoxalines can be achieved in some cases under forcing conditions[220].

This can be rationalised as an effect of resonance delocalisation of the positive charge: One canonical form of the monosubstituted quinoxalinium ion leaves the positive charge on the non-quaternised nitrogen. Resonance dequaternisation of the complexing nitrogen atom in structure (XIX) would give rise to an analogous situation, and might be expected to lead to a reduction in the basicity of the remaining nitrogen.

The observed infrared spectra exclude the possibility that the species formed is, in fact, an intermediate of the type (XX)



(XIX)



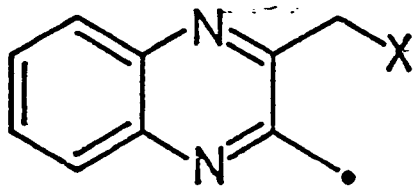
(XX)

Carbonyl region i.r. spectroscopy cannot distinguish between structures (XVIII) and (XIX), but the stoichiometry of the reaction appears to suggest disubstitution.

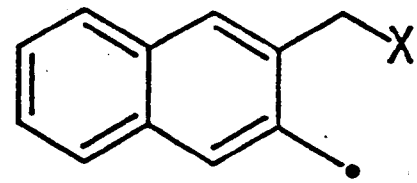
The intermediate decomposes over a few hours to yield 2,3-dimethylquinoxaline as, by far, the major product. No carbonylated products were detected.

The reason for the greater tendency for cobalt-carbon bond homolysis in the quinoxaline derivative than in the naphthalene case is not clear. It seems unlikely that resonance stabilisation

should be much greater for radical (XXI) than for radical (XXII).



(XXI)



(XXII)

The strength of the CH_2 - H bond in toluene is about 327 kJ mol^{-1}, while that in α-picoline is 314 kJ mol^{-1} [221].

In addition, the preferred form of the derivative produced by the reaction of 2,3-bis-(bromomethyl)-quinoxaline with tetracarbonylcobaltate(1-) is the acyl, (XVIII), which bears no direct CH_2 - Co liaison. It would be expected that the acyl carbonyl group would act as a protecting group against homolysis.

SECTION THREE : THE REACTIONS OF BIFUNCTIONAL ACYL HALIDES WITH TETRACARBONYLCOBALTATE(1-)

With the exception of methyl iodide, simple alkyl halides have been found to react poorly or not at all with tetracarbonylcobaltate[183]. For this reason, attempts to form cobalt carbonyl derivatives of alkanes were confined to acyl, rather than alkyl systems.

Isomerisation of acyl cobalt tetracarbonyls has been reported by Takegami and co-workers[207]. Takegami illustrates that whereas isomerisation tends to be from branched to straight chain acyls, the reverse reaction is also possible. Takegami also points out[222] that the isomerisation reaction is promoted by the presence of a polar (basic ?) solvent and inhibited by the presence of an atmosphere of carbon monoxide.

For these reasons, and for the reasons outlined in the

preceding chapter, interest was confined to terminal acyls and the later reactions were carried out in benzene or toluene under one atmosphere of carbon monoxide.

In the formation of 2,6-dimethylheptan-4-one from iso-valeryl chloride (p.72), there was no evidence to suggest that isomeric ketones had been formed.

Sebacoyl chloride, $ClOC(CH_2)_8COCl$, reacts with two moles of tetracarbonylcobaltate to give an intermediate with infrared absorptions at 2110 cm^{-1} (medium intensity, sharp), 2060 cm^{-1} (shoulder), 2025 cm^{-1} (strong), 1999 cm^{-1} (strong) and 1712 cm^{-1} (m). This is consistent with the formation of an approximately trigonal bipyramidal intermediate with the alkacyl group in an axial position [cf 63a]. The shoulder at 2060 cm^{-1} can be assigned as the axial carbonyl stretch. The band of medium intensity at 2110 cm^{-1} is due to the totally symmetric stretching mode of the equatorial carbonyl groups. The out of phase stretching modes of the equatorial carbonyl groups give rise to absorptions at 2025 cm^{-1} and at 1999 cm^{-1}. The fact that these two modes are non-degenerate indicates that the arrangement of the equatorial carbonyl groups deviates significantly from trigonal symmetry[209]. The band at 1712 cm^{-1} arises from the stretch of the acyl carbonyl group. Although the acyl carbonyl band is featured, in no case could splitting of the band be detected. (This is true, also, of the acyl bands of the phosphine derivatives of the intermediate, the spectra of which were recorded in n-pentane). This indicates either that rotational isomerism (of the Co-C (acyl) bond) does not occur, or that the acyl modes of the rotamers are accidentally degenerate[cf 223].

Addition of two moles of triphenylphosphine per mole of intermediate gives rise to a species absorbing at 2044 cm^{-1} (medium), 1977 cm^{-1} (strong) and 1955 cm^{-1} (strong). This indicates replacement of a carbonyl group[183] (the axial cf [209]) by PPh_3. The acyl carbonyl stretch is displaced to 1677 cm^{-1}.

The spectrum of the triphenylphosphine derivative in n-pentane shows two very strong, well resolved bands of approximately equal intensity at 1985 cm^{-1} and at 1963 cm^{-1}. A much weaker band is present at 2051 cm^{-1}, and a broad, medium intensity band is present at 1685 cm^{-1}.

At high temperatures, for example in refluxing diglyme, $(OC)_4CoCO(CH_2)_8COCo(CO)_4$ decomposes to 1,7-octadiene. No evidence of isomeric dienes was found.

At lower temperature, the species decomposes without giving rise to carbonylated products. The destination of the hydrocarbon backbone is unknown, although the possibility of some form of polymerisation must be considered.

Adipoyl chloride (1,6-hexandioic acid dichloride) reacts analogously with tetracarbonylcobaltate to give an intermediate with i.r. absorptions at 1999 cm^{-1} (v.s.), 2022 cm^{-1} (v.s.), 2060 cm^{-1} (sh), 2106 cm^{-1} (m). The ν_{acyl} band is extremely broad and has maximum intensity at 1708 cm^{-1}.

Heating this intermediate to 40 ^{o}C for a few days gives rise to another cobalt carbonyl species. The spectrum, which does not show any signs of change in relative intensities of the bands with time, resembles those reported for hexadecacarbonylhexacobalt[103,224].

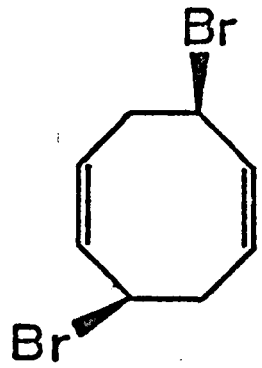
This species slowly (~2 days) decomposed in benzene at 70 °C.

Once again, the products of the decomposition of the acyl intermediate are uncharacterised. A very small amount of carbonylated product was formed in one of these reactions, but a proton n.m.r. signal at about 9.8 δ (in $CDCl_3$) indicated that this was almost certainly an aldehyde formed by reaction between the acyl cobalt tetracarbonyl and some $HCo(CO)_4$ which may have been present[183].

The ready formation of five membered ring ketones observed in the preceding section appears to be dependent on the presence of the aromatic grouping. It seems likely that the function of the aromatic ring is to act as a template, constraining the two reacting centres to be fairly close together. In an unconstrained situation, other modes of decomposition may be preferred.

SECTION FOUR : THE REACTION OF TETRACARBONYLCOBALTATE(1-) WITH CIS, CIS - 3,7-DIBROMOCYCLO-OCTA-1,5-DIENE

Another unsuccessful attempt to bring about cyclisation resulted from the thermal decomposition of the product of the reaction of z , z - cis, cis - 3,7-dibromocyclo-octa-1,5-diene (XXIII) with tetracarbonylcobaltate(1-).



(XXIII)

The cyclic dibromide reacts with tetracarbonylcobaltate at 40 °C in toluene or benzene under one atmosphere of CO to yield a species with i.r. absorption at 2055 cm^{-1} (strong) and 1982 cm^{-1} (v. strong) (2053 and 1978 cm^{-1} in THF). This indicates that the product contains a (η^3-allyl) $Co(CO)_3$ type fragment.

Thermolysis of the intermediate at 40 °C in C_6D_6 gives no evidence of the production of carbonylated species. In several cases, a weak, broad peak at 5.85 δ was noted in the n.m.r. of the product mixture. In one case, a very broad, very weak signal stretching from ~3.0 δ to ~0.5 δ was noted. It is possible, therefore, that some bicyclo [5.1.0] octa-2,5-diene (3,4-homotropilidine, XXVI) was formed in the reaction [225].

The experiment was repeated in d_8 toluene in order that a low temperature n.m.r. investigation could be made. In this case however, the peak at 5.85 δ was barely perceptible, and the expected resolution of the extremely broad band of 3,4-homotropilidine could not be detected.

In the light of the observations in section two of this chapter,

it does not seem unreasonable to assume that the Co-C bond in the π-allyl cobalt tricarbonyl intermediate suffers homolysis. The product of this homolysis would be a resonance stabilised allyl radical of the type (XXV). It is possible to envisage two pathways for the formation of homotropilidine (figure 23). No n.m.r. evidence was found for the formation of 1, 3a, 4, 6a-tetrahydropentalene[225] (XXVII).

Although figure 23 illustrates a reaction involving disubstituted species, it is not certain that the intermediate bears two cobalt atoms at any one time. The simplicity of the i.r. spectrum implies that there is no Co-Co liaison in intermediate[216]. This almost certainly means that if the intermediate is, in fact, the disubstituted species (XXIV), then the cobalt atoms must lie above opposite faces of the ring. The formation of such a species would arise from one S_N2 attack by $Co(CO)_4^-$ on a halogen-bearing carbon preceded by, or followed by, one S_N2' attack on an allylic carbon.

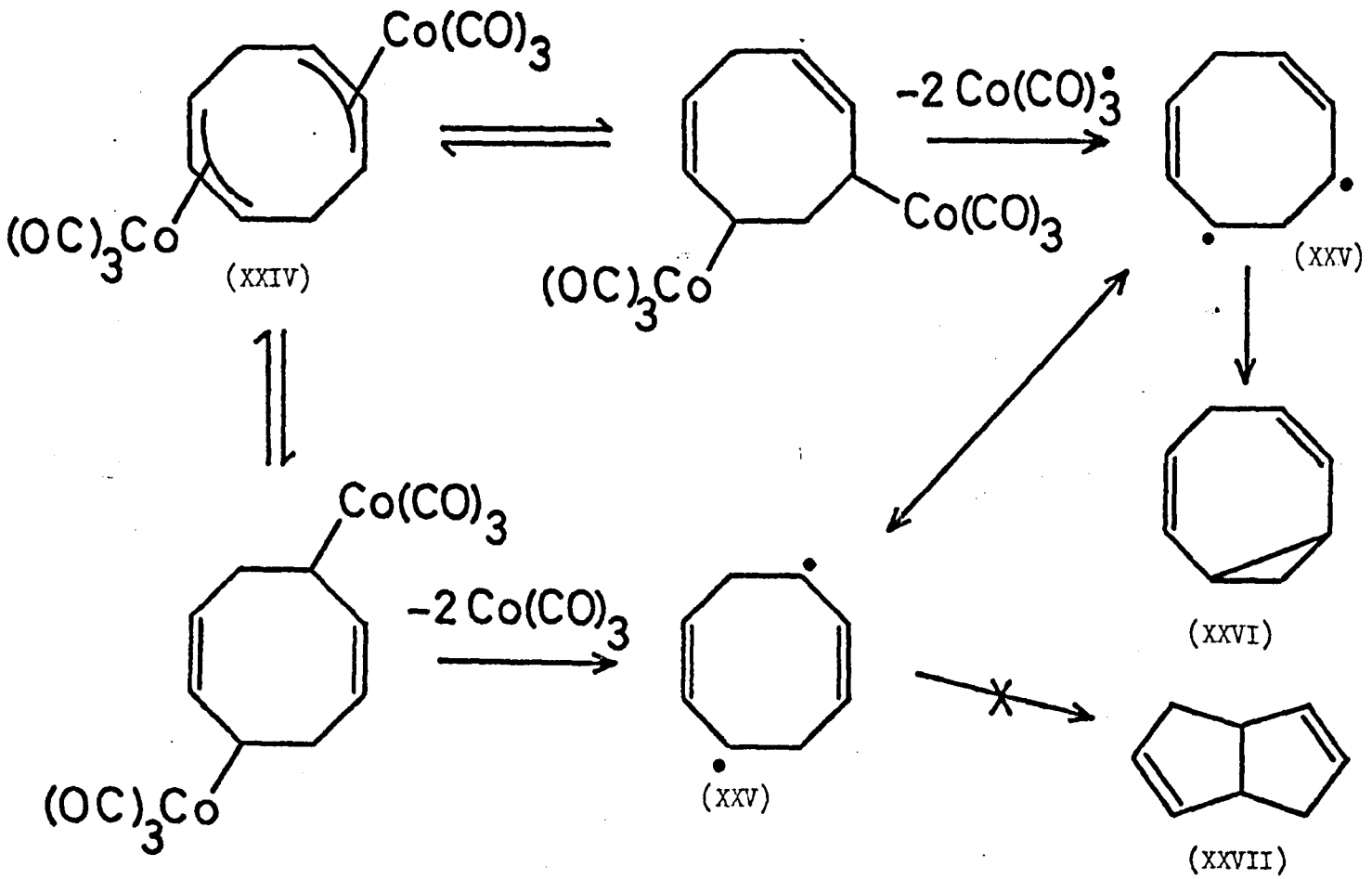


figure 23

following page 111.

SECTION FIVE : EXPERIMENTAL

A) Materials and General Procedures

The general procedures regarding preparation, purification and drying of reagents, solvents, gases and glassware described in chapter 2 apply to the reactions in this chapter. Ethereal solvents were distilled directly into reaction vessels in equipment similar to that illustrated in figure 20.

Infrared spectra, except where otherwise stated, were recorded on a Perkin-Elmer 577 double beam spectrometer in RIIC FH-01 cells with synthetic sapphire windows. Reaction solvent was used as a reference.

Proton magnetic resonance spectra, except where otherwise stated, were recorded in $CDCl_3$ on a Varian T-60 (60 MHz) spectrometer. It was necessary to remove all metallic species prior to n.m.r. analysis. This was achieved by the method used in the work-up of g.l.c. samples (vide infra).

Gas-liquid chromatography was carried out on a Pye 104 chromatograph equipped with a flame ionisation detector and a chromalog integrator.

The column, a six foot, 4 mm internal diameter glass coil, was washed with chlorotrimethylsilane in order to substitute polar groups on the glass surface[226].

A batch of Gaschrom Q (100 - 120 mesh) was coated with OV-1 to give 10% by weight of the liquid phase. The methyl silicone gum was applied by carefully evaporating the solvent from a suspension of

the support material in a solution of OV-1 in redistilled methylene chloride. The procedure was repeated several times to ensure even distribution of the liquid phase.

A plug of Me_3SiCl-treated glass wool was inserted into one end of the coil. This end was attached to a water pump. The 10 % OV-1 absorbed Gaschrom Q was packed into the column at reduced pressure. Another plug of Me_3SiCl-washed glass wool was inserted to contain the support material.

The column was attached to the sampling inlet of the chromatograph. The column was heated to 170 °C and purged with helium at this temperature for 24 hours in order to remove undesired volatiles.

During storage, the column ends were sealed by rubber septa.

The column was found to contain about 5,400 theoretical plates, where the number of theoretical plates, N, is given by the following equation:

$$N = 4 \left(\frac{\text{distance from injection to peak maximum (mm)}}{\text{peak width at 0.606 peak height (mm)}} \right)^2$$

This was found to be sufficient to completely resolve a mixture containing benzyl bromide, 1,2-diphenylethane, diphenylmethane and dibenzyl ketone without recourse to temperature programming.

Reaction product mixtures required extensive pre-treatment prior to sampling: Inorganic cobalt species were to be avoided since these could clog the column, or coat the support. Organometallic species posed a greater potential problem, since

these would certainly have decomposed at the high temperatures involved, leaving metallic, or other inorganic cobalt species, and organic moieties (including CO). These organic species, being formed on the column, would appear unpredictably at the detector and severely complicate, or obliterate the chromatogram.

On conclusion of the reactions, therefore, a few ml. of concentrated HCl were added to the reaction vessel. (A downstream bromine water-bubbler ensured the destruction of any $HCo(CO)_4$ in the exhaust gas.) The mixture was stirred for a few hours, in order to allow complete oxidation of the cobalt carbonyls. Any residual alkyl- or acyl- cobalt tetracarbonyls which may have been present at this stage would have been converted to aldehydes. After ensuring, by i.r., the absence of $HCo(CO)_4$, the inorganic Co^{II} species were removed by ether/acid and ether/water separations. The ethereal layers were dried over $MgSO_4$, filtered and taken up into solution in a known amount of analar acetone. G.l.c. samples were withdrawn from this solution.

N.m.r. analysis of the worked-up reaction mixture generally allowed identification of the materials present in the product mixture. Standard solutions of each suspected component were injected into the column in order to determine the relationship between the area under a chromatogram peak and the quantity of material represented by this. Excellent linear relationships were found for all compounds studied. The positions of the peaks in the standard chromatograms offered a check that the n.m.r. assignments had been correct.

The accurate volume of a given sample solution could be

determined from the area of a peak due to n-decane. This alkane was added to the acetone reservoir to serve as an internal standard.

Thin layer chromatography was employed as a preliminary analytical technique and on a preparative scale.

One metre x 20 cm x 1 mm preparative plates were prepared by spreading a suspension of kieselgel G in water onto the plate. The plates were activated by placing in an oven, and leaving at 125 ^{o}C overnight.

It was found necessary to redistil the eluent (usually CH_2Cl_2 or toluene) prior to use to remove traces of hydrocarbon oils.

The plates were developed by masking off several strips of the plate and spraying these with a developer. A solution of 2,4-dinitrophenylhydrazine in ethanol and HCl was used to detect ketones and aldehydes. Other materials were detected by using volatilised iodine or by spraying with a solution of ceric sulphate in dilute sulphuric acid. This last developer requires the application of heat. This was supplied to the developed strip by means of a hair dryer. All of these development procedures were carried out in a fume hood.

The positions of products on the plate could be extrapolated from the developed strips. The products were removed (neglecting the developed parts of the plate) and separated from the silica by dissolution in redistilled methylene chloride and filtration.

20 cm x 20 cm x 1 mm preparative plates were made up in the same way, except that about 10 % by weight kieselgel GF_{254} was added to the silica. Illumination of the plates with light of the correct wavelength allowed determination of the positions of the bands.

10 cm x 20 cm x 0.25 mm analytical plates were made up in a similar manner, and developed chemically as above. Micro-t.l.c. plates for more routine analyses were prepared by dipping microscope slides into a slurry of silica gel in chloroform.

Column chromatography was carried out in apparatus similar to that illustrated in figure 24.

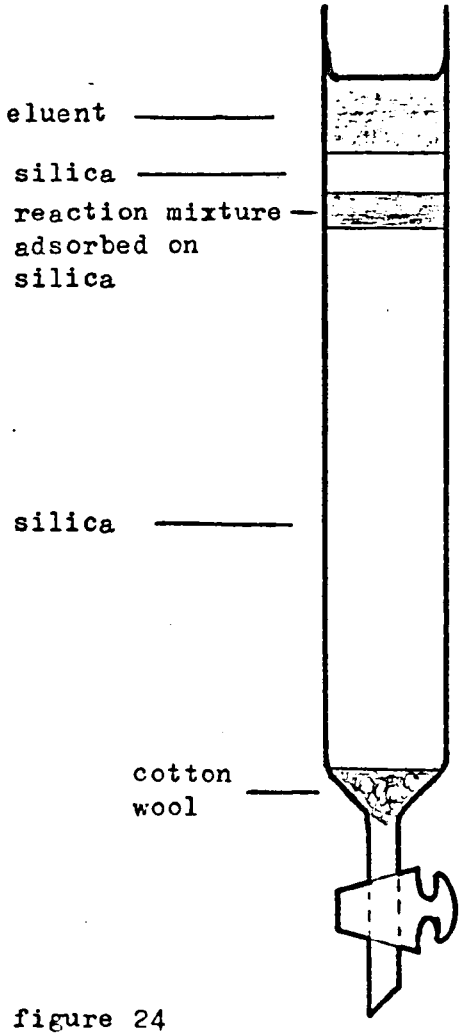


figure 24

The reaction mixture was adsorbed onto a small amount of silica by careful evaporation of the solvent. The procedure was repeated to ensure even distribution of the mixture. Filter papers and a small amount of silica were placed atop the column to prevent disturbance on adding the eluent.

Fractions were analysed by routine t.l.c. (typically four or five fractions were analysed per single micro-t.l.c. plate). Fractions containing a given component were combined, filtered to

remove silica, and evaporated ready for n.m.r. analysis.

Immobile material could be removed by methylene chloride extraction from the silica of the dissembled column.

B) The Experiments

1) The formation and thermal decomposition of benzyltetracarbonylcobalt(I) in tetrahydrofuran

The apparatus illustrated in figure 20 was set up and purged with dried, oxygen-free nitrogen. 0.4408 g $Co_2(CO)_8$ and ~1 g anhydrous $CoCl_2$ were deposited in the reaction vessel.

0.4 ml freshly distilled benzyl bromide was syringed into the vessel. The formation of $PhCH_2Co(CO)_4$ and $PhCH_2COCo(CO)_4$ was monitored by i.r., as was the change in the position of the equilibrium between the two on application of one atmosphere of CO.

The temperature was increased to 60 °C. The conversion of $PhCH_2COCo(CO)_4$ to $PhCH_2Co(CO)_4$ and the decomposition of the latter were monitored by i.r. After 7 hours at 60 °C, the reaction mixture was allowed to cool to room temperature. An analytical t.l.c. (toluene eluent) showed one dominant and several minor components. The major product gave a bright golden spot at R_f 0.35 when sprayed with 2,4-dinitrophenylhydrazine solution.

The reaction mixture was adsorbed onto a few grams of silica as described in section A). The volatiles removed at this stage were inspected by n.m.r. and found to contain a small amount of toluene. A column separation was carried out. Only one component proved to be present in sufficient quantity to allow n.m.r. investigation. The n.m.r. obtained showed a singlet at 3.45 δ

and a featured single band at about 7.15 δ. The ratio of the integrals of these signals was approximately 2:5. The spectrum was superimposable with that of an authentic sample of 1,3-diphenylpropan-2-one (dibenzyl ketone). 0.1498 g of the yellow oil was collected indicating a yield of 42 % based on starting benzyl bromide. The 2,4-dinitrophenylhydrazine derivative of the product melted sharply at 110 °C (lit.[228] 110 °C).

A similar reaction carried out under one atmosphere of nitrogen gave dibenzyl ketone in 29 % yield.

The yield from another reaction, under one atmosphere CO, was deduced by comparing the height of the 3.54 δ signal in the n.m.r. of the reaction mixture with that in the spectra of a number of standard solutions of dibenzyl ketone. (The reaction mixture had been treated to remove cobalt species as in section A). The yield of dibenzyl ketone indicated by this method was 39 %.

2) <u>The reaction of benzyl bromide with tetracarbonylcobaltate(1-) in benzene</u>

An oven-dried three-necked round-bottomed flask was equipped with a gas inlet, a rubber septum cap, a magnetic stirrer bar and a water condenser topped by a gas outlet. The assembly was purged with dried oxygen-free nitrogen and then with dried carbon monoxide.

0.7252 g $Co_2(CO)_8$ was deposited in the vessel against a countercurrent of CO. 50 ml of a benzene solution of $[K(\text{dicyclohexyl-18-crown-6})]_2[CoBr_4]$ ($\sim 5 \times 10^{-3}$ M), followed by 0.3 ml freshly distilled benzyl bromide were syringed into the vessel.

After 23 hours, an i.r. showed the presence of $PhCH_2Co(CO)_4$. Some $Co_4(CO)_{12}$ had also been formed.

The temperature was increased to 50 °C. After 40 hours at this temperature, the i.r. absorptions due to $PhCH_2Co(CO)_4$ had disappeared, and the i.r. spectrum comprised a weak band at 1710 cm^{-1} in addition to the spectrum of $Co_4(CO)_{12}$.

The reaction mixture was worked up and a g.l.c. analysis carried out as in section A).

The proton n.m.r. of the reaction mixture had suggested the presence of benzyl bromide, 1,2-diphenylethane and diphenylmethane in addition to dibenzyl ketone. G.l.c. confirmed that these were, to all intents, the only species present. (Two very weak peaks were noted at long retention time). N.m.r. analysis of the volatiles removed during the work-up indicated the presence of some toluene.

Standard solutions containing various amounts of the four identified components were injected into the column at 170 °C (Sampler temperature = 220 °C) and graphs relating the weight of a given species added to the area of that species' chromatogram peak drawn up. (The detector sensitivity was found to vary from compound to compound.)

An aliquot of the reaction mixture was injected under exactly the same conditions. From the area of the chromatogram peaks, the weight of each species present was deduced. From the area of the peak due to n-decane, the accurate volume of the aliquot could be calculated. Thus, the total weight of each species formed in the

reaction were deduced.

In this case, it was found that dibenzyl ketone was formed in 69 % yield, 1,2-diphenylethane 23 %, diphenylmethane 4 % and unreacted benzyl bromide 4 %. Assuming roughly equivalent detector sensitivities (a gross approximation : vide supra), the two long retention time species combined represented less than 1 % starting benzyl bromide.

In an exact repeat of the above reaction, 0.5563 g $Co_2(CO)_8$ and 0.5 ml freshly distilled benzyl bromide were allowed to react under one atmosphere CO in 125 ml of benzene containing approximately 5 x 10^{-3} molar $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2[CoBr_4]$.

The products of the reaction were separated by toluene elution down a silica column. The reaction mixture was found to contain 0.0786 g benzyl bromide, 0.0442 g Ph_2CH_2, 0.0102 g $PhCH_2CH_2Ph$ and 0.2725 g $(PhCH_2)_2CO$. These weights represent yields of 7 % diphenylmethane, 3 % 1,2-diphenylethane and 69 % dibenzyl ketone, based on reacted $PhCH_2Br$. The destination of the remaining 20 % of the benzyl groups is not known, although some toluene was detected during work-up.

The difference in the relative yields of 1,2-diphenylethene and diphenylmethane is attributed to the difference in concentration of phenyl radicals in the two reactions.

3) <u>The reaction of benzyl bromide with octacarbonyldicobalt in benzene in the absence of disproportionating agents.</u>

0.1238 g $Co_2(CO)_8$ and 0.2 ml freshly distilled benzyl bromide in 25 ml sodium-dried benzene under one atmosphere of dried oxygen-

free nitrogen at 25 °C showed no tendency to react over a period of 24 hours. Inspection of i.r. spectra recorded after this time showed no sign of $PhCH_2Co(CO)_4$ or of $Co(CO)_4^-$. Some degree of conversion of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ had occurred.

0.1069 g $Co_2(CO)_8$ was dissolved in 25 ml dried benzene under one atmosphere dried oxygen-free nitrogen in a reaction vessel similar to that described in 2) above. 0.2 ml of twice-distilled $PhCH_2Br$ was syringed into the reaction vessel. The contents of the vessel were heated until the benzene refluxed. After three hours reflux, an i.r. spectrum indicated the presence of benzyl cobalt tetracarbonyl and, perhaps, of (η^3-benzyl)-cobalt tricarbonyl. Continued heating over 16 hours destroyed the intermediates: A peak at 1710 cm^{-1} in the i.r. indicated the presence of dibenzyl ketone.

The reaction mixture was filtered to reveal a green-blue solid and a yellow-green solution. The electronic spectrum of the green solution was recorded in the region 400 - 700 nm.

The resistance of a 1 cm cube of the solution was measured by means of a dip cell connected to a 1.6 kHz A.C. Wheatstone bridge. The value obtained, 6×10^{12} ohms compared with 6×10^{13} ohms for 'pure' benzene and 2.5×10^{12} ohms for a 5×10^{-3} molar solution of $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2[CoBr_4]$ in benzene. The higher conductivity in the green solution than in 'pure' benzene may have been significant, but all of the values obtained were close to the limiting value for the bridge circuit. Consequently, the values should be treated with some scepticism.

The reaction mixture was worked up as in section A) and a g.l.c. analysis performed as in 2) above. This indicated the presence of benzyl bromide (56% based on starting $PhCH_2Br$), Ph_2CH_2 (5 %), $PhCH_2CH_2Ph$ (11 %) and $(PhCH_2)_2CO$ (24 %). Indicating yields of 11 % diphenylmethane, 24 % 1,2-diphenylethane and 54 % dibenzyl ketone based on reacted benzyl bromide.

4) The reaction of α,α′ - dibromo-o-xylene with tetracarbonylcobaltate (1-)

A reaction vessel of the type described in 2) above was set up and purged with dried, oxygen-free nitrogen, followed by carbon monoxide.

0.2467 g α,α′ -dibromo-o-xylene and 0.5795 g $Co_2(CO)_8$ were placed together in the vessel. 25 ml benzene containing approximately 5 x 10^{-3} molar $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2[CoBr_4]$ was syringed in.

After one hour at room temperature, little change was observed in the infrared spectrum of $Co_2(CO)_8$. The temperature was increased to 60 °C. After 90 minutes at this temperature, a substantial decrease in the $Co_2(CO)_8$ concentration was evident. Infrared bands due to the alkyl cobalt carbonyl intermediate were detected at 2105 cm^{-1} and 2010 cm^{-1}. A weak absorption was noted at 1755 cm^{-1}.

After 17 hours at room temperature, an i.r. showed the presence of a peak at 1755 cm^{-1} in addition to the spectrum of $Co_4(CO)_{12}$.

Dodecacarbonyltetracobalt was destroyed by hydrochloric acid as in section A), and the organic products separated by means of an

ether-water separation. The brown-yellow oil revealed proved to be largely composed of a single component: An analytical t.l.c. (toluene eluent) showed a dominant d.n.p. positive spot with several minor iodine positive species at higher and lower R_f.

A proton n.m.r. of the oil showed a strong singlet at 3.4 δ and a broader signal at 7.2 δ in the integral ratio 1:1. This spectrum, as well as the i.r. spectrum proved to be identical with the spectra of an authentic sample of indan-2-one.

5) The reaction of 2,3-bis-(bromomethyl)-naphthalene with tetracarbonylcobaltate in THF

2.3161 g anhydrous $CoCl_2$ and 1.6030 g $Co_2(CO)_8$ were placed in the reaction vessel of apparatus similar to that illustrated in figure 20 under one atmosphere N_2.

About 150 ml THF was distilled into the vessel. After valence disproportionation was complete, the THF reservoir was removed and replaced by a reflux condenser topped by a nitrogen outlet. The existing nitrogen outlet was replaced by a nitrogen inlet. The assembly was purged for one hour by a stream of carbon monoxide.

1.0182 g 2,3-bis-(bromomethyl)-naphthalene was added. An infrared spectrum recorded 24 hours after the addition showed that the cobalt tricarbonyl intermediate,(XVII), had formed. No $Co_2(CO)_8$ or $Co(CO)_4^-$ were in evidence. A weak band at 1758 cm^{-1} indicated the presence of some ketonic product.

The exact positions of the bands in the spectra of this novel intermediate were pinpointed by recording a spectrum of the reaction mixture at this stage on a Perkin-Elmer 5080 spectrometer in cells

with KBr windows. The spectrum was calibrated using carbon monoxide. Weak absorptions in the carbon-bromine stretching region could be assigned to the presence of a small amount of unreacted starting material.

15 ml of the mixture was placed in a round-bottomed, three-necked flask under one atmosphere of nitrogen. Excess triphenylphosphine was added. Slow gas evolution was noted. I.r. showed that the triphenylphosphine derivative formed overnight at room temperature.

The vessel containing the remainder of the reaction mixture was cooled to -78 ^{o}C for three hours, but no evidence for the formation of a tetracarbonyl species was found on inspection of the i.r.

The mixture was heated to reflux for twelve hours. The colour changed from green to blue during this time. An infrared spectrum recorded at this time showed that the intermediate had been destroyed, but reconstituted tetracarbonylcobaltate was present in addition to the material absorbing at 1758 cm^{-1}.

The THF was evaporated and about 50 ml analar toluene added. The toluene extracts were filtered and evaporated. 0.4421 g of a fairly crystalline milky-brown solid was collected. A nujol mull i.r. spectrum of this solid showed a very intense peak at 1750 cm^{-1}. A proton n.m.r. revealed a very complex series of aromatic-region signals. Strong singlets were present at 3.64 δ and at 2.35 δ in the integral ratio $\sim$2:3. The former signal is in a similar position to the aliphatic proton signal from indan-2-one,

indicating that the product may be 1,3-dihydro-(2H)-benz-[f]-inden-2-one. The latter is exactly superimposable with the methylene signal from 2,3-dimethylnaphthalene.

A column separation was carried out on some of the solid. A column of internal diameter 4 cm. approximate bed volume 370 ml was used. The column was eluted with distilled toluene. 5 ml fractions were collected and analysed by t.l.c.

The fractions of standard eluted volume 1.35 to 1.76 were collected. The solvent was evaporated to reveal a white powder. Sublimation of this material at reduced pressure gave 0.160 g of a highly crystalline white solid melting at 105 °C (lit.[229] for 2,3-dimethylnaphthalene, 105 °C).

The fractions of standard eluted volume 2.31 to 3.73 (the chromatographic behaviour of this product is discussed later) were collected and evaporated to reveal a yellow oil. Recrystallisation from methanol gave 0.086 g of a yellowish solid which decomposed at 85 °C. Analysis gave 85.95 % C, 5.73 % H (calc. for $C_{13}H_{10}O$: 85.69 % C, 5.53 % H). The mass spectrum (A.E.I. MS 12) of the solid showed the parent ion at m/e 182. The most intense feature in the spectrum is at m/e 154, probably arising from the $(parent-CO)^+$ ion.

The solid reverted to a tacky, yellow-brown oil on standing. This behaviour is reminiscent of that of indan-2-one[230].

6) The reaction of 2,3-bis-(bromomethyl)-naphthalene with tetracarbonylcobaltate in benzene

A reaction vessel was equipped as in 2) above and purged with oxygen-free, dried nitrogen followed by carbon monoxide.

1.7279 g $Co_2(CO)_8$ was deposited in the vessel and 40 ml benzene containing 0.275 mmole $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2[CoBr_4]$ syringed in.

A substantial degree of valence disproportionation was noted by i.r. over 24 hours at room temperature. 1.0471 g 2,3-bis-(bromomethyl)-naphthalene was added. An infrared spectrum recorded after stirring the solution at room temperature overnight showed that the $(\eta^3\text{-allyl})Co(CO)_3$ intermediate, (XVII), had been formed.

At this stage, 15 ml of the reaction mixture was withdrawn and syringed into another reaction vessel of similar design. To this was added 0.8 ml trimethylphosphite. (In another experiment: triphenylphosphite was used). The formation of the trimethylphosphite derivative was monitored by i.r., and was found to be complete after 68 hours at room temperature.

The remaining 25 ml of the reaction mixture was heated to 60 °C. The decay of the peaks due to the intermediate, and the appearance of a band at 1758 cm^{-1} were monitored on i.r. After 116 hours at 60 °C, no intermediate remained.

The mixture was allowed to cool to room temperature and a benzene-water separation carried out. The organic layer was washed with water until no blue colouration remained. The organic layers

were dried over $MgSO_4$, filtered and evaporated to reveal a yellow solid which turned brown on standing in air.

A proton n.m.r. spectrum of the solid showed numerous peaks, none of which corresponded to the signal previously observed for 1,3-dihydro-(2H)-benz-[f]-inden-2-one at 3.64 δ. The two strongest features in the spectrum were singlets at 3.52 and 3.49δ. Other peaks were present at 4.77 δ(unreacted 2,3-bis-(bromomethyl)-naphthalene), 3.15 and 2.36δ.

(In another, similar experiment, the same range of signals was observed, except that in this case, a signal at 3.64 δ was present while that at 3.49 δ was absent).

The peak at 2.36 δ is assigned to 2,3-dimethylnaphthalene, while that at 3.15 δ was found to be exactly co-incident with the methylene signal from 1,2-dihydrocyclobuta-[b]-naphthalene.

A preparative scale (20 cm x 20 cm x 1 mm) t.l.c. was carried out. The plate was eluted with toluene. A fraction of very high R_f was collected. N.m.r. analysis proved this fraction to consist of a mixture of 2,3-dimethylnaphthalene and 1,2-dihydrocyclobuta-[b]-naphthalene. (A small scale, narrow-bore column separation of these two components was attempted, but insufficient material was collected to allow characterisation).

Another fraction revealed a small amount of light brown crystalline solid. This material sublimed, and on collection gave a highly crystalline solid melting at 105 °C. The proton n.m.r. confirmed that this was 2,3-dimethylnaphthalene.

The lowest fraction, which gave a yellow colour on spraying

with 2,4-dinitrophenylhydrazine solution, consisted of a band of $R_f \sim 0.2$ with substantial tailing back to the base line. The material above the base line was collected and another t.l.c. carried out. This gave a d.n.p. positive band of R_f 0.25, with little tailing. The base line material was collected. Another t.l.c. performed on this gave a d.n.p. positive band of R_f 0.25 with very severe tailing.

An n.m.r. spectrum of the d.n.p. positive fractions collected from above the base line in these t.l.c.'s showed a complex aromatic region (Figure 25) as well as a strong singlet at 3.66 δ. The ratio of the integrals of the two areas of absorption was approximately 3:2.

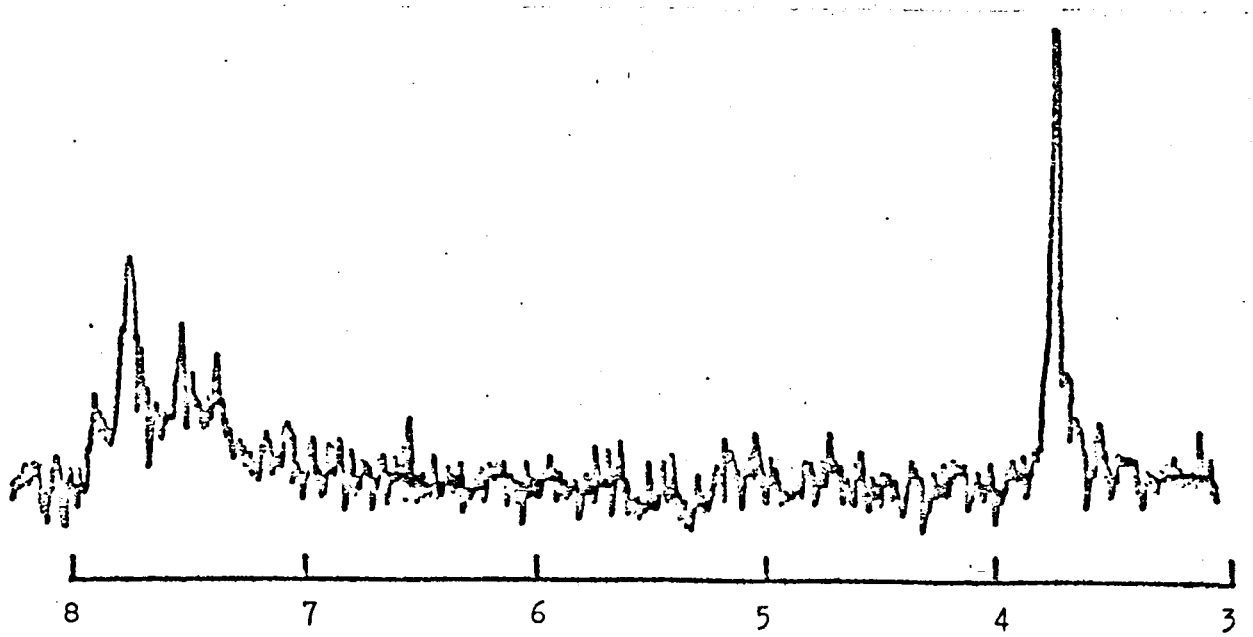


Figure 25: The ^1H n.m.r. spectrum of 1,3-dihydro-(2H)-benz-[f]-inden-2-one. The scale represents downfield shift (parts per million) from the internal standard, tetramethylsilane.

The remainder of the plate was searched, without success, for materials giving rise to n.m.r. singlets at 3.52 or 3.49 δ.

It is tentatively suggested that 1,3-dihydro-(2H)-benz-[f]-inden-2-one forms a complex with some cobalt species. (Cations containing ketones complexed to divalent cobalt have been claimed[231]) The presence of the paramagnetic cobalt centre causes a change in the position of the n.m.r. signal from that of the free ketone cf [232, 233]. The complex, which may be immobile in the silica/toluene system is slowly broken down during chromatography and the freed ketone is then eluted.

0.0987 g 1,3-dihydro-(2H)-benz-[f]-inden-2-one was isolated. This indicates a yield of 26 % based on starting 2,3-bis-(bromomethyl)-naphthalene. Comparison of the intensities of the 4-proton methylene singlets in the n.m.r. spectrum of the reaction mixture indicates the following yields (based on 1,3-dihydro-(2H)-benz-[f]-inden-2-one = 26 %): 2,3-bis-(bromomethyl)-naphthalene 52 %; 1,2-dihydrocyclobuta-[b]-naphthalene 12 %, 2,3-dimethylnaphthalene 5 %. This implies yields, based on reacted dibromide of 54 % ketone, 25 % 1,2-dihydrocyclobuta-[b]-naphthalene and 10 % 2,3-dimethylnaphthalene. The destination of the remaining 11 % of the startin· bromide is unknown. By analogy with the reaction of benzyl bromide, it would not be unrealistic to assume that at least some 2-benzyl-3-methyl naphthalene and perhaps some 2,3-dibenzylnaphthalene, were formed.

7) The reaction of 2,3-bis-(bromomethyl)-quinoxaline with tetracarbonylcobaltate (1-)

0.8666 g $Co_2(CO)_8$ and about 3 g K_2CoBr_4 were deposited in the

reaction vessel of the apparatus illustrated in figure 20 under one atmosphere of nitrogen. About 60 ml THF was distilled into the vessel.

About 30 minutes later, the reaction mixture was blue. 0.5407 g 2,3-bis-(bromomethyl)-quinoxaline was added. An i.r. spectrum recorded 30 minutes later showed that the cyclic intermediate, (XVIII) or (XIX) had formed.

The intermediate decayed overnight at room temperature leaving the 1884 cm^{-1} band due to reformed tetracarbonylcobaltate as the only significant feature in the i.r. spectrum.

THF was removed at reduced pressure and a preparative scale (20 cm x 20 cm x 1 mm) t.l.c. performed. Elution with CH_2Cl_2 revealed that one major product had been formed. The main band (R_f 0.18) yielded 0.1715 g of a white solid melting at 103-4 ^oC. The proton n.m.r. of this material showed a quinoxaline-type aromatic region and a strong singlet at 2.76 δ (integral ratio 41:62). This n.m.r. is co-incident with that of an authentic sample of 2,3-dimethylquinoxaline. (lit.[234] melting point 104.5 - 105.5 ^oC).

A small amount (0.068 g) of unreacted 2,3-bis-(bromomethyl)-quinoxaline was isolated from a band at R_f 0.45.

The reaction was repeated in toluene : 0.2908 g 2,3-bis-(bromomethyl)-quinoxaline and 0.1508 g $Co_2(CO)_8$ were deposited in a round-bottomed, 3-necked flask under one atmosphere of CO. 40 ml toluene approximately 5 x 10^{-3} molar in $[K(\text{dicyclohexyl-18-crown-6})]_2[CoBr_4]$ was injected. An i.r.

spectrum recorded two hours later showed a distinct distortion of the spectrum due to $Co_2(CO)_8$ in the region of 2050 cm^{-1}, other peaks were evident at 1994 cm^{-1}, 1962 cm^{-1} and at 1694 cm^{-1}. This was taken as evidence for the formation of the cyclic intermediate, (XVIII) or (XIX). After 48 hours at room temperature, the bands due to the intermediate had disappeared, and $Co_4(CO)_{12}$ remained as the only cobalt carbonyl species.

A t.l.c. with methylene chloride eluent revealed the presence of some unreacted starting material. A fraction of R_f 0.18 proved to contain 0.0282 g 2,3-dimethylquinoxaline. This represents 20 % of the starting dibromide.

In all cases involving the reaction between 2,3-bis-(bromomethyl)quinoxaline and cobalt carbonyls, an intense red colour formed. The species giving rise to the red colour did not give rise to absorption in the carbonyl stretching region of the i.r., was air stable, and apparently quite soluble in organic solvents. The red material was eluted unpredictably in t.l.c.s. Often apparently very pure samples (M.Pt.) of 2,3-dimethylquinoxaline obtained from this reaction were coloured red. This indicates that the colour arises from a very small amount of a very strong chromophore.

8) The reaction of 1,8-octanedioic acid dichloride (sebacoyl chloride) with tetracarbonylcobaltate(1-)

0.3961 g $Co_2(CO)_8$ was deposited in the reaction vessel of the apparatus illustrated in figure 20. About 50 ml THF was distilled in. After 22 hours at room temperature, an i.r. was recorded and

this showed that valence disproportionation had gone to completion.

0.15 ml sebacoyl chloride was syringed into the reaction vessel. After three hours at room temperature, an i.r. spectrum indicated the presence of an acyl cobalt tetracarbonyl species. The 1785 cm^{-1} band due to sebacoyl chloride was completely absent, but a peak at 1735 cm^{-1} indicated that some ester had been formed (chapter 2).

After a further two hours, 0.425 g PPh_3 was added to the reaction mixture. Rapid gas evolution was noted and an i.r. recorded after one hour showed that complete conversion to the PPh_3 derivative had occurred.

Several attempts were made to isolate the PPh_3 derivative, but none of these yielded an analytically pure sample: The organocobalt species decomposed on silica, even when steps were taken to exclude oxygen. Thus, chromatography was of no value. After a long series of ether /n-pentane extractions and washings, some orange plates were collected. The nujol mull i.r. spectrum of this solid shows little sign of impurity. However, a proton magnetic resonance spectrum of the material proved to be very severely broadened by the presence of paramagnetic species. Microanalysis gave 61.39 % C and 3.45 % H (required for $C_{52}H_{46}Co_2O_8P_2$; C 63.81 %, H 4.74 %). It is believed that aerial oxidation to divalent cobalt had occurred (some triphenylphosphine oxide was detected in the washings).

In a similar experiment, $(OC)_4CoCO(CH_2)_8COCo(CO)_4$ was prepared from 1.1736 g $Co_2(CO)_8$ and 0.45 ml sebacoyl chloride in about 200 ml diglyme under one atmosphere of nitrogen.

The diglyme reservoir was removed and replaced by a reflux condenser topped by a nitrogen outlet. The existing outlet was replaced by a gas inlet.

The solution was refluxed (160 °C) for 4½ hours. An i.r. spectrum recorded after this time revealed that whereas some absorption in the 2000 cm^{-1} region was to be seen, extensive decarbonylation had occurred.

The diglyme solution was distilled into a cold trap surrounded by solid CO_2:(no ether solubles, except diglyme, were discovered in the residues.) An ether water separation was carried out: The diglyme water mixture was extracted with four portions of diethyl ether. The ether layers were then washed with 5 portions of water. The ether fractions were dried over $MgSO_4$, filtered and evaporated to reveal a mobile, colourless liquid. The n.m.r.[235] and i.r. spectra [236] of this material are those of 1,7-octadiene. The liquid boiled at 112 - 117 °C at atmospheric pressure (lit. [237] 116 °C).

1,7-octadiene appears to be the only significant product of the reaction.

In similar experiments, the organocobalt intermediate was decomposed at lower temperatures (from 45 - 67 °C). In no case were ketonic or aldehydic products detected. Indeed, it proved impossible to extract identifiable organic products from the reaction mixtures.

0.5218 g $Co_2(CO)_8$ and 0.5 ml sebacoyl chloride were added to a reaction vessel containing 25 ml benzene approximately 5 x 10^{-3} M

in $[K(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2\ CoCl_4$ under one atmosphere of CO. After 18 hours at room temperature an i.r. indicated that about half of the acyl halide remained unreacted. A further 0.5985 g $Co_2(CO)_8$ was added as a solution in 50 ml benzene. An i.r. recorded three hours later indicated that all of the sebacoyl chloride had been consumed. The spectrum also showed that excess $Co_2(CO)_8$ remained.

Heating the solution to 40 °C for 90 minutes caused conversion from the acyl to the alkyl tetracarbonyl (complete disappearance of the band at 1712 cm^{-1}, the most intense band is now at 2009 cm^{-1}; sharp band at 2105 cm^{-1}). The alkyl cobalt intermediate was observed to decay over a few days at 55 °C. Again, however, the products of the decomposition could not be identified.

9) The reaction of butanedioic acid dichloride (adipoyl chloride) with tetracarbonylcobaltate (1-)

$(OC)_4CoCO(CH_2)_4COCo(CO)_4$ was formed from adipoyl chloride and tetracarbonylcobaltate in benzene in a manner analogous to the formation of $(OC)_4CoCO(CH_2)_8COCo(CO)_4$ in hydrocarbon solvent. Formation of $HCo(CO)_4$ proved to be a much greater problem in this case than in the reaction of sebacoyl chloride despite the fact that adipoyl chloride was distilled shortly before use.

Again, no products of the thermal decomposition could be isolated. In many cases, a yellow spot appeared on spraying the t.l.c. of these reaction mixtures with 2,4-dinitrophenylhydrazine, but a weak signal at 9.8 δ in the n.m.r. of the worked-up reaction mixture indicated that an aldehyde rather than a ketone had been formed.

10) The reaction of z,z-cis,cis -3,7-dibromocyclo-octa-1,5-diene with tetracarbonylcobaltate (1-).

A round bottomed, three-necked flask equipped as in 2) above was purged with nitrogen and then with CO. The gas outlet led to a cold trap at -78 °C before passing on to the nujol, bromine water, nujol bubbler series.

0.1045 g $Co_2(CO)_8$ and 0.7 g K_2CoBr_4 were deposited in the reaction vessel and 20.0 ml toluene containing 0.1517 g dicyclohexyl-18-crown-6 was added by syringe. After stirring overnight, 0.0535 g z,z-cis,cis-3,7-dibromocyclo-octa-1,5-diene was added. No sign of the formation of organocobalt species was indicated by i.r. after 20 hours at room temperature. The mixture was stirred at 40 °C for 22 hours. At the end of this time, a π-allyl type intermediate was observed in the i.r. Continued heating (4 days) at this temperature removed all absorptions between 2200 and 1600 cm^{-1}. A toluene-water separation was carried out and the organic layer dried over $MgSO_4$.

A proton n.m.r. of the mixture showed the presence of no species other than toluene and dicyclohexyl-18-crown-6.

A proton n.m.r. of the trapped volatiles showed these to consist solely of toluene.

The apparatus illustrated in figure 26 was evacuated and filled with nitrogen several times to remove oxygen. 0.0239 g $Co_2(CO)_8$, 0.0383 g dicyclohexyl-18-crown-6, 0.1114 g K_2CoBr_4 and 0.0239 g z,z-cis,cis-3,7-dibromocyclo-octa-1,5-diene were deposited in the reaction limb under one atmosphere of nitrogen.

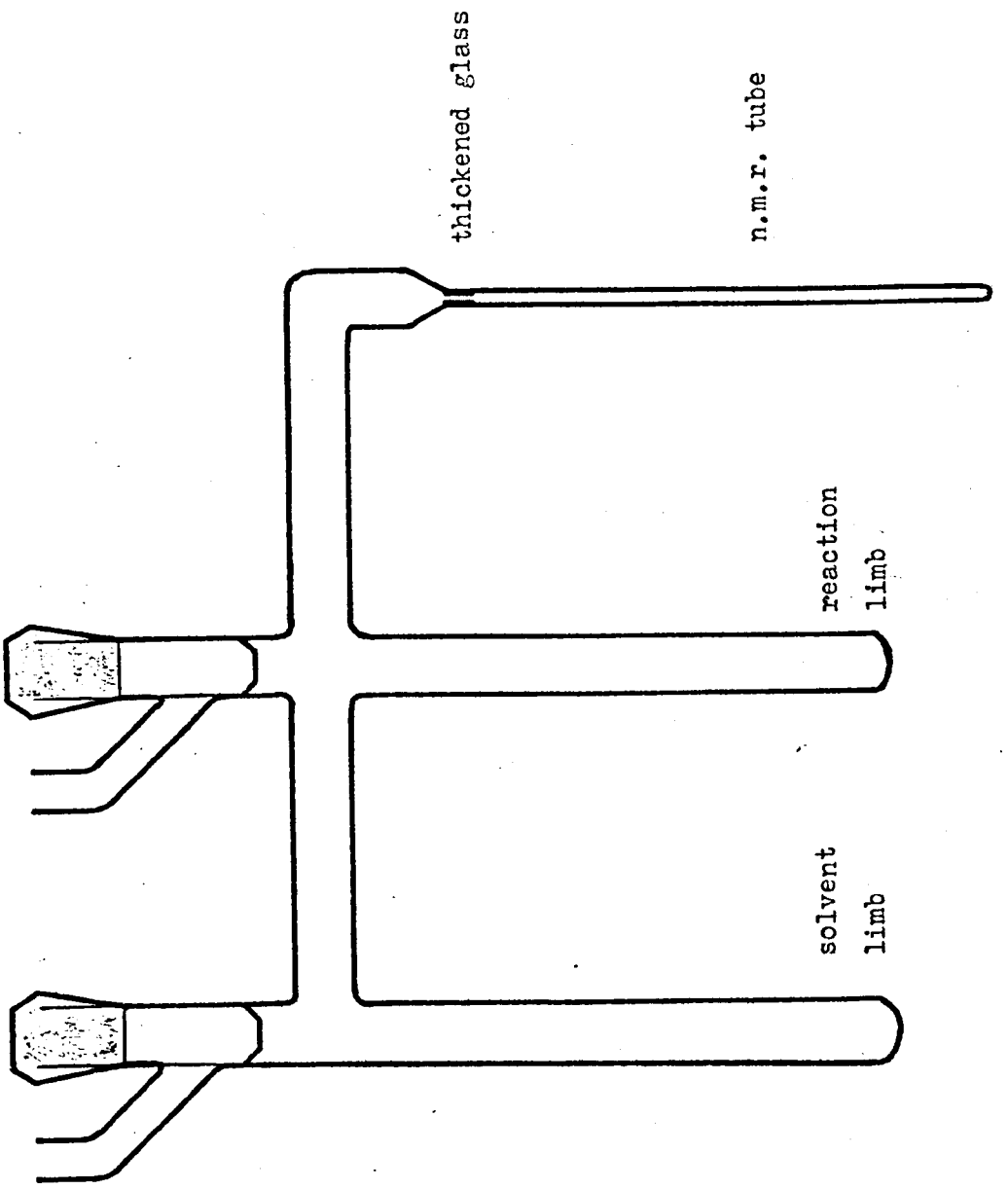


figure 26

following page 135.

About 1.5 ml hexadeuterobenzene was added to the solvent limb together with about 0.01 ml tetramethylsilane.

While applying liquid nitrogen flasks to both limbs, the vessel was evacuated. The taps were closed and the benzene and t.m.s. distilled into the reaction limb. Upon thawing, a deep green colour emerged in solution. On standing overnight, the mixture became blue. This was taken to indicate the complete valence disproportionation of $Co_2(CO)_8$ to a colourless salt of tetracarbonylcobaltate (1-).

The temperature of the reaction limb was increased to 40 °C. The mixture became green overnight. The green colour gradually disappeared, and after four days at 40 °C, the mixture was again blue.

The reaction limb was cooled to -196 °C, and the non trapable volatiles vented to the vacuum line. The trapable volatiles were distilled into the n.m.r. tube. The n.m.r. tube was sealed and severed from the apparatus while the contents of both were maintained at -196 °C.

The 60 MHz proton n.m.r. showed what was taken to be the 35 °C (the probe temperature) spectrum of 3,4-homotropilidine in addition to a weak signal at 7.2 δassigned to some proton-containing benzene.

Extraction of the residues with $CDCl_3$ gave a blue solution. The blue colour was removed by shaking with water. The deuterochloroform layer was dried over $MgSO_4$ and filtered. An n.m.r. of the residue, a white wax, showed this to be essentially

dicyclohexyl-18-crown-6, although a very weak absorption was noted at 5.85δ.

The reaction was repeated in octadeuterotoluene to allow a low temperature study of the n.m.r. In this case, however, the signal at 5.85 δwas exceedingly weak. The sample was cooled to -50 °C in the probe of a JEOL 60 HL spectrometer, and although this caused changes in the spectrum around 2 δ, signals from proton-substituted solvent and from spinning-side bands of tetramethylsilane made identification of these changes impossible.

SECTION SIX : SUMMARY OF THE CARBONYL STRETCHING FREQUENCIES OF SPECIES ENCOUNTERED DURING THIS WORK

The spectra of the organocobalt species encountered during this work are classified in tables 12 to 15 according to the number and idealised arrangement of the carbonyl groups. The spectra of some of these species have been reported: The references listed in the final column of each table indicate these species, but the spectral frequencies listed in the tables are those observed in this work.

Table 12: Acyl cobalt tetracarbonyls

Species	a_1(eq)	a_1(ax)	e(eq)	ν_{acyl}	solvent	Comments
$(OC)_4CoCO(CH_2)_8COCo(CO)_4$	2110	2060	2025,1999	1712	THF	
$(OC)_4CoCO(CH_2)_8COCo(CO)_4$	2106	2060	2022,1999	1708	C_6H_6	
$(CH_3)_2CHCH_2COCo(CO)_4$	2105	a	2023,2005		C_6H_6	
$(CH_3)_2CHCOCo(CO)_4$	2105	a	2020,2000	1690	THF	b,cf 183
$PhCH_2COCO(CO)_4$	2112	2058	2030,2005	1735	THF	
$PhCHCH_3COCo(CO)_4$	2108	2040	2020,2004	~1690	THF	c
$PhCH_2CH_2COCo(CO)_4$	2106	2040	2020,2004	~1710	THF	d

Notes a) Band obscured by the presence of other carbonyl species.

b) It cannot be stated with certainty that this species had not isomerised to $CH_3CH_2CH_2COCo(CO)_4$

c) (α-bromoethyl)-benzene + tetracarbonylcobaltate(1-) after 2 hours 30 minutes at room temperature.

d) (α-bromoethyl)-benzene + tetracarbonylcobaltate after 114 hours at room temperature (vide infra)

Table 13: Acyl cobalt tricarbonyl triphenylphosphines

Species	a_1	e	acyl	solvent
$(Ph_3P)(OC)_3CoCO(CH_2)_8COCo(CO)_3(PPh_3)$	2044	1977,1955	1677	THF
" " " " "	2051	1985,1963	1685	n-pentane

Table 14: Alkyl cobalt tetracarbonyls

Species	a_1(eq)	a_1(ax)	e (eq)	solvent	
$(OC)_4Co(CH_2)_8Co(CO)_4$	2105	a	2009	C_6H_6	
$PhCH_2Co(CO)_4$	2102	2058	2014	THF	
$PhCH_2Co(CO)_4$	2100	2055	2010	C_6H_6	
$o\text{-}C_6H_4[CH_2Co(CO)_4]_2$	2105	a	2010	C_6H_6	
$PhCHCH_3Co(CO)_4$		a	2007	C_6H_6	b

Notes a) Band obscured by the presence of other carbonyl species

b) It cannot be stated with certainty that this species had not isomerised to $PhCH_2CH_2Co(CO)_4$.

Table 15: (η^3-allyl) cobalt tricarbonyls, $YCo(CO)_3$

Y	a	e	solvent	comments
$CH_2CH\ CH_2$	2064	1989	toluene	cf 206
$CH_2\ CH\ CH_2$	2062	1989	THF	"
$CH_3\ CH_2\ CH\ CH_2$	2059	1982	THF	cf 201
$C_6H_5\ CH_2$	2052	1985	C_6H_6	
½(2,3-dimethylnaphthyl)	2047	1991	THF	
½(cyclo-octa-1,5-dienyl)	2055	1982	toluene	
½(cyclo-octa-1,5-dienyl)	2053	1978	THF	

Table 16: (η^3-allyl) cobalt dicarbonyl-phosphines and phosphites

Y $Co(CO)_2$ Z

Y	Z	a	b	solvent	Comments
$CH_2\ CH\ CH_2$	PPh_3	1990	1934	THF	cf 206
½(2,3-dimethylnaphthyl)	PPh_3	1970	1914	THF	
$CH_2\ CH\ CH_2$	$P(OPh)_3$	2018	1958	toluene	cf 202
½(2,3-dimethylnaphthyl)	$P(OPh)_3$	2010,2000	1970,1959	C_6H_6	
½(2,3-dimethylnaphthyl)	$P(OMe)_3$	2000,1989	1940	C_6H_6	

Other systems: a) Intermediate formed in the reaction of tetracarbonylcobaltate with 2,3-bis-(bromomethyl)-quionoxaline: 2050 (a_1,eq), 1994 (a_1,ax), 1961 (e, eq), 1691 (acyl)

b) Species formed following the thermal decomposition of $(OC)_4CoCO(CH_2)_4COCo(CO)_4$: 2108 (w), 1986 (w), 2058 (v.s.), 2043 (s), 2021 (m) and 1751 (m). Compare $Co_6(CO)_{16}$ 224.

All frequencies in this section are given in reciprocal centimetres.

CHAPTER FOUR

THE CHEMICAL CLEAVAGE OF AIKYL- AND ACYL-COBALT TETRACARBONYLS

CHAPTER FOUR : THE CHEMICAL CLEAVAGE OF ALKYL- AND ACYL-COBALT TETRACARBONYLS

SECTION ONE : INTRODUCTION

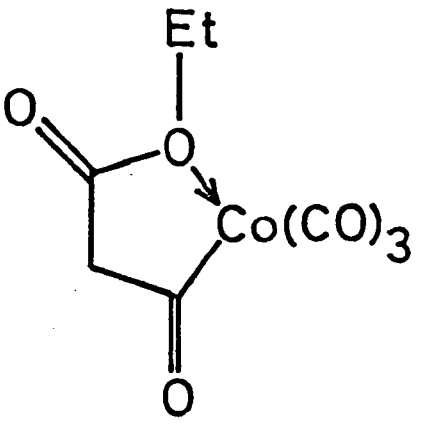
The result of an attack by a nucleophile on organocobalt carbonyls depends to a great extent on the nature of the base as well as on the nature of the carbonyl.

Where the nucleophile concerned has π-acid character, a ligand substitution reaction may occur: (η^3-allyl.) $Co(CO)_3$ is known to lose one co-ordinated carbonyl group on reaction with trialkylphosphines [205]. Acyl cobalt tetracarbonyls react similarly to form the acyl cobalt tricarbonyl trialkylphosphine [205]. The same product is formed in the reaction of alkyl cobalt tetracarbonyl with trialkylphosphine. In these last two cases, trialkylphosphine co-ordinates to the intermediate, $RCOCo(CO)_3$ formed in equilibrium (35b) or (8) [238].

Nucleophiles not necessarily recognised as π-acceptors have been shown to attack alkylpentacarbonylmanganese(I) to give the nucleophile-substituted acyl tetracarbonylmanganese species. For example, primary and secondary amines attack methylpentacarbonylmanganese(I) to give acetyl(amine)tetracarbonyl-manganese(I)[239].

The analogous reaction of non-π-accepting nucleophiles with acyl- and alkyl- cobalt tetracarbonyls does undoubtedly occur, but this has been observed only in the special case where the product is a 5-membered cyclic acyl cobalt tricarbonyl. For example, carboethoxyacetyl cobalt tetracarbonyl undergoes an intramolecular

substitution reaction, in which an oxygen atom replaces a co-ordinated carbonyl group to give an intermediate of the type (XXVIII) [183].



(XXXVIII)

The formation of the cyclic derivative (XVIII) in chapter three of this work serves as another illustration of this reaction.

In general, however, primary and secondary amines react with alkyl- or acyl- cobalt tetracarbonyls to give amides. Alcohols react analogously to give esters [160]. These reactions can occur intramolecularly to give 5- and 6- membered lactams and lactones [172].

It would appear that the preferred net reactions of alcohols and amines with alkyl- and acyl- cobalt tetracarbonyls are alcoholysis and aminolysis respectively. Oxygen- or nitrogen- base substitution for carbonyl at the cobalt centre occurs only where the geometry of the intermediate forbids the alcoholysis or aminolysis. Since there are no reports of intermolecular self-

alcoholysis or aminolysis of β-hydroxylalkyl or β-aminoalkyl cobalt tetracarbonyls, it is possible that the formation of metallacycles in these cases relies on a template effect. The formation of a relatively strain-free chelate ring may also be important in these particular cases [cf 240]. It can be argued however, that this factor is not a determining one, since the geometrically plausible six-membered metallacycle is not observed. following the cobalt carbonyl catalysed carbonylation of allylamine. Instead, 2-pyrrolidone is formed [172].

Alcoholysis is slow at room temperature, but the rate of the process is considerably enhanced by the presence of sodium alkoxide [160]. The anilinolysis of phenylacetyl cobalt tetracarbonyl required 20 hours at 35 °C [160].

The base catalysed alcoholysis of both 1-octanoyl- and 2-octanoyl-cobalt tetracarbonyl have been shown to proceed without isomerisation of the alkyl group when the reaction is performed below 50 °C [160].

The precise mechanism of the alcoholysis reaction has not been discovered. The result appears to be the same as that of a classical nucleophilic attack on the acyl carbonyl group. Since the possibility of involvement of the cobalt centre obviously exists, it would be dangerous to state, without further evidence, that the two mechanisms are directly analogous.

SECTION TWO : THE ALCOHOLYSIS AND AMINOLYSIS OF HYDRATROPYL-TETRACARBONYLCOBALT(I)

Benzyl chloride reacts with tetracarbonylcobaltate (1-) in THF, in the presence of aniline to give phenylacetanilide in 47 % yield [160].

We have substantially increased this yield by adding aniline to a preformed sample of benzylcobalt tetracarbonyl in THF or benzene. It is evident that reaction between aniline and benzyl chloride claims more potential product than does thermal decomposition of the organocobalt intermediate.

The formation of the anilide can be described by either of the equations (40) or (41).

$$PhCH_2Co(CO)_4 + CO \rightleftharpoons PhCH_2COCo(CO)_4 \qquad \text{(40a)}$$

$$PhCH_2COCo(CO)_4 + PhNH_2 \longrightarrow PhCH_2CONHPh + HCo(CO)_4 \qquad \text{(40b)}$$

$$PhCH_2Co(CO)_4 + PhNH_2 \longrightarrow PhCH_2CONHPh + HCo(CO)_3 \qquad \text{(41a)}$$

$$HCo(CO)_3 + CO \longrightarrow HCo(CO)_4 \qquad \text{(41b)}$$

(The reaction was carried out under one atmosphere of carbon monoxide).

$HCo(CO)_4$ was never detected in reaction mixtures following reaction between aniline and alkylcobalt tetracarbonyls. It is to be assumed that the strongly acidic [241] hydrocarbonyl reacts instantaneously with unreacted aniline to give anilinium tetracarbonylcobaltate. The tetracarbonylcobaltate anion was observed to be produced in the anilinolysis of benzyl cobalt tetracarbonyl in benzene. (This does not of itself imply that the salt, anilinium tetracarbonylcobaltate is soluble in benzene, since a metathesis reaction can occur with the solubilised halide used as a catalyst in the first step of the reaction).

(α-Bromoethyl)-benzene reacts with tetracarbonylcobaltate under one atmosphere of carbon monoxide at room temperature to yield a product with infrared absorptions at 2108 cm^{-1} (m), 2040 cm^{-1} (sh), 2023 (s), 2004 (s) and ~1690 cm^{-1}(w). This is consistent with the

formation of an acyl cobalt tetracarbonyl intermediate of the type (XXIX)

$$PhCHCH_3COCo(CO)_4 \qquad (XXIX)$$

The thermal decomposition (40 °C) of this intermediate in THF leads to the formation of a huge number of products. No rigorous analysis of the product mixture was attempted, but ethylbenzene and at least two carbonylated products, one of these an aldehyde, were formed. A small amount of hydridotetracarbonylcobalt(I) was detected in a 'downstream' cold trap. The involvement of this species explains the production of an aldehyde [183]. The most probable origin of this hydrocarbonyl is its β-elimination from 1-phenylethyltetracarbonylcobalt (I). The other product of this reaction is styrene. Styrene itself was not detected in the reaction mixture, and so the possibility of oligomerisation of this product must be considered. It can be assumed that ethylbenzene is formed by homolysis of a cobalt-carbon bond followed by hydrogen radical abstraction from THF.

The acyl cobalt intermediate reacts very slowly with aniline in THF. (The reaction required more than 48 hours at room temperature.) Several products were formed, but by far the major of these was hydrocinnamanilide (3-phenylpropionanilide, (XXX)), which was formed in 70 % yield based on starting (α-bromoethyl)-benzene. No evidence of the formation of hydratropanilide (2-phenylpropionanilide, (XXXI)) was found

$PhCH_2CH_2CONHPh$ (XXX)

$PhCH(CH_3)CONHPh$ (XXXI)

The formation of (XXX) illustrates isomerisation from a

branched- to a straight- chain acyl cobalt tetracarbonyl [207].

Octacarbonyldicobalt is rapidly disproportionated in methanolic solutions. The rate of the reaction is enhanced by the presence of cobaltous halide. Addition of (α-bromoethyl)-benzene under one atmosphere of carbon monoxide to a solution of tetracarbonylcobaltate (1-), formed in this manner, gives rise to absorptions in the infrared spectrum at 2108 cm^{-1} (m), 2040 (m, sh), 2020 (s, sh) and 2004 (s) cm^{-1}. A very weak, broad absorption is present around 1700 cm^{-1}. Addition of a solution of sodium methoxide after five hours at room temperature immediately destroys the organocobalt species. Analysis of the reaction mixture shows that the only products of the reaction are methyl-(2-phenylethyl) ether and methyl hydratropate (methyl 2-phenylpropionate). The formation of the ether, by direct reaction between methoxide and (α- bromoethyl)-benzene indicates that the formation of the acyl tetracarbonyl intermediate had by no means gone to completion after 5 hours at room temperature. (α-Bromoethyl)-benzene reacts with methanol in the absence of added base, but this reaction was found to take several days at room temperature. Cobalt halides do not significantly catalyse the reaction.

Three explanations of the observation that no isomerised product is formed following base catalysed methanolysis of (XXIX) while only isomerised product results following reaction of the same intermediate with aniline may be advanced:

a) That attack on the non-isomerised intermediate is electronically preferred (whether or not this is true depends on the balance of the inductive and resonance effects at the carbonyl carbon of the non-isomerised intermediate) but that steric

hindrance allows methoxide, but not aniline, to attack this site.

b) That the isomerisation process is slow, and that the strongly nucleophilic methoxide anion reacts completely prior to extensive isomerisation. The poorer nucleophile, aniline can react only to a very limited extent before the non-isomerised intermediate disappears. (The two isomers may, in fact, reach an equilibrium, but by analogy with other alkyl- and acyl- cobalt tetracarbonyl systems, the hydrocinnamyl tetracarbonyl is expected to be the strongly preferred partner [222]).

c) The aniline in some way promotes the isomerisation process, whereas methoxide does not.

Addition of a solution of sodium phenoxide to a solution of (XXIX) in toluene brings about fairly slow decomposition of the acyl cobalt intermediate. Several minor products, including phenyl hydrocinnamate are formed but by far the major products are phenyl hydratropate and phenyl (1-phenylethyl) ether.

The reaction between hydratropyl cobalt tetracarbonyl and sodium t-butoxide in THF takes about 5 days to complete at room temperature. Complete analysis of the extremely complex product mixture was not attempted, but both t-butyl hydratropate and t-butyl hydrocinnamate were produced in very low yields.

These results imply that steric effects are important only insofar as they play a role in determining the nucleophilicity of the attacking base: An extremely hindered base, t-butoxide is capable of displacing the tetracarbonylcobaltate anion from (XXIX) Phenoxide, which has almost identical steric character to aniline

reacts, under suitable conditions, to give phenyl hydratropate as the major of the ester products. (The formation of the ether, $PhCH(CH_3)OPh$ in the latter case indicates that once again, completion of the formation of (XXIX) was not complete when the base was added.)

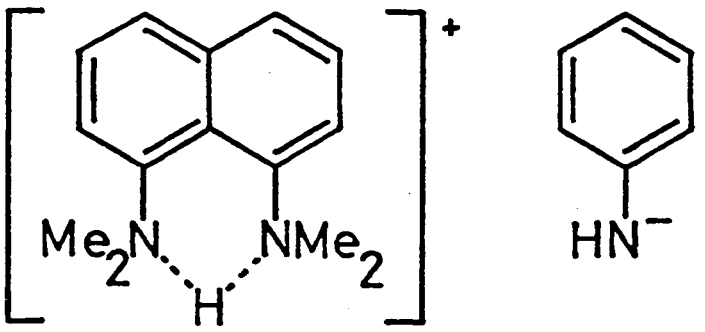
A THF solution of hydratropyl cobalt tetracarbonyl was prepared and allowed to stand at room temperature, under one atmosphere of carbon monoxide for 114 hours. The infrared spectrum of the intermediate was monitored throughout this time (vide infra).

Addition of a solution of sodium methoxide in methanol brought about complete destruction of the intermediate within 30 minutes. By far the major product of the reaction was methyl hydrocinnamate.

The indication seems to be that slow isomerisation of hydratropyl cobalt tetracarbonyl to hydrocinnamyl cobalt tetracarbonyl occurs in THF at room temperature. This isomerisation process is not dependent, or at least, not totally dependent on presence of added base. (This work does not eliminate the possibility that a base such as aniline may enhance the rate of the isomerisation). After a period of two or three days, substantially all of the acyl cobalt intermediate exists in the straight chain form. Nucleophilic attack can occur at the acyl carbonyl group of either isomeric intermediate, and the rate of this attack, at least in gross terms, appears to depend on the classical nucleophilicity of the base.

1,8-Bis-(N,N-dimethylamino)-naphthalene ('proton sponge')

abstracts a proton from aniline to give the salt (XXXII).



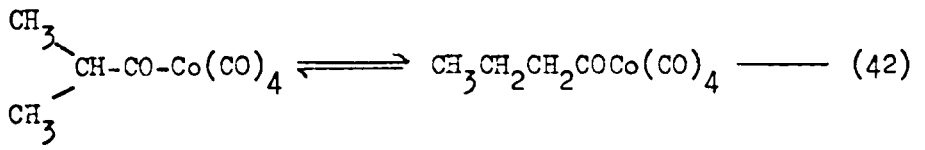
(XXXII)

Addition of a solution of this salt to hydratropyl cobalt tetracarbonyl in THF causes comparatively rapid decomposition of the acyl:(XXX) and (XXXI) are formed in approximately equal yields.

It is, therefore, possible to synthesise the amide, (XXXI), from (α-bromoethyl)-benzene, aniline and carbon monoxide in the presence of tetracarbonylcobaltate. The main drawback of the reaction appears to be that formation of the intermediate (XXIX) takes so long to go to completion, that isomerisation of some of the hydratropyl cobalt tetracarbonyl is sure to take place prior to the addition of the base. Presence of the base prior to formation of the acyl tetracarbonyl intermediate allows reaction between the base and the unreacted (α-bromoethyl)-benzene.

Takegami [222] has observed that no isomerisation of iso-butyryl cobalt tetracarbonyl occurs at 25 °C in benzene solution under 1 atm. CO, while very substantial isomerisation of this species is observed over a few hours in diethyl ether, ethyl acetate and dioxan under one atmosphere of carbon monoxide. Takegami has

related this to the inhibition of the equilibration process, rather than a shift in the equilibrium, (42), since n-butyryl cobalt tetracarbonyl shows the same reluctance to isomerise in benzene, and a limited propensity to isomerise in the other solvent systems.



(42)

When attack by aniline on hydratropyl cobalt tetracarbonyl occurs in benzene, the reaction takes over 45 hours to complete. In this case, however, (XXX) and (XXXI) are produced, once again, in approximately equal yields. The dominance of the non-isomerised product in the reaction involving phenoxide was no doubt enhanced by the fact that this reaction was performed in toluene (vide supra).

It is proposed that the yield of the non-isomerised product could be maximised by adding an anilide salt to a solution of (XXIX) in hydrocarbon solvent under increased carbon monoxide pressure.

At first sight, the carbonyl region infrared spectra of the two intermediates appear to be superimposable. On closer inspection, however, the weak acyl stretching band can be seen to migrate from about 1690 cm^{-1} to about 1710 cm^{-1} in THF. Using the simplistic model of aliphatic and benzylic ketones, this is the expected effect of substituting an aliphatic for a benzylic group attached to the carbonyl: That this picture is simplistic is shown by the fact that phenylacetylcobalt tetracarbonyl has a substantially higher acyl stretching frequency than do simple aliphatic acyl cobalt tetracarbonyls (cf. chapter 3, section 6). Whereas the terminal carbonyl stretches appear to be basically unperturbed by the isomerisation, a slight change to lower frequency (of no more than

two or three wavenumbers) is observed in the totally symmetric equatorial stretch. The sense of this change agrees with the observed frequencies for the corresponding band in the spectra of phenylacetyl cobalt tetracarbonyl and the aliphatic acyl cobalt tetracarbonyls (chapter 3, section 6).

SECTION THREE : EXPERIMENTAL

A) Materials and General Procedures

All solvents and gases were purified and dried as in the preceding chapters. THF was distilled directly into reaction vessels. Aniline was distilled until all traces of colour were removed.

Sodium alkoxides were prepared by adding metallic sodium to the corresponding alcohol, either using the alcohol itself as a solvent or employing THF, benzene or toluene as a diluent or solvent.

Products of the reactions were recognised in some cases by isolation and characterisation, but more routinely, by comparison of their n.m.r. spectra with those of authentic samples of suspected products.

Ethers, such as methyl (1-phenylethyl) ether, were prepared by reaction of the alkyl halide ((α-bromoethyl)-benzene) with the required sodium alkoxide (NaOMe) in solution either in the corresponding alcohol or in an inert solvent.

Hydrocinnamic acid (3-phenylpropionic acid) was prepared by the sodium/mercury amalgam reduction of cinnamic acid [242]. Purity of the product was checked by n.m.r. and by melting point. (44-45 °C

after recrystallising from ether, lit. 46 - 47 °C [243]).

The esters of hydrocinnamic- and hydratropic acid (2-phenylpropionic acid) were prepared via the acyl halides. $PhCH_2CH_2COCl$ and $PhCH(CH_3)COCl$ were formed from the acids and thionyl chloride under one atmosphere of dried nitrogen. The method of Buckles and Cooper [244] was followed in order to avoid the possibility of condensation reactions.

Alcoholic, or hydrocarbon solutions (suspensions) of sodium alkoxides were added in situ at 0 °C. After removal of the volatiles, an organic phase/aqueous base separation was carried out, apparently without ester hydrolysis. The purity of the products was checked by n.m.r.

Anilides were formed in a similar manner. Freshly distilled aniline was added to the recently formed acyl halides under one atmosphere of nitrogen. After removal of the volatiles, a small amount of aqueous hydrochloric acid was added and an organic phase/aqueous acid separation carried out. Recrystallisation from petroleum ether gave $PhCH(CH_3)CONHPh$ M.Pt. 132-4 °C (lit. 133-4 °C [245]) $PhCH_2CH_2CONHPh$. M.Pt. 94 - 96 °C (lit. 97 °C [246]).

The n.m.r. spectra of the hydrocinnamic and the hydratropic backbones are very readily distinguishable. The spectra of the aliphatic protons of hydratropic acid and its esters and anilide all conform to the simple, first order AX_3 type of spectrum. A one-proton quartet appears at about 4 δ, and a three-proton doublet arises between 1.5 and 2.0 δ. In the case of the phenyl ester, slight splitting is observed on all six signals.

Hydrocinnamic acid and its esters and anilide have a second order A_2B_2 type of spectrum centred in the region of 3.0 δ. The anilide and, to a lesser extent, the methyl ester show a slight degree of resolution. The spectra of these two are, however, still decidedly A_2B_2 in character. The four main signals in the aliphatic region of the spectrum of hydrocinnamanilide are at 3.06, 2.98, 2.78 and 2.70 δ.

The hydratropic acid and the (α-haloethyl)-benzenes were in all cases used direct and assumed to be racemic mixtures of the dextro- and laevo- rotatory isomers.

All reactions involving cobalt carbonyls were carried out under one atmosphere of carbon monoxide in a good spark-proof fume hood. The reactions were monitored by inspecting the infrared spectra of aliquots of the reaction mixture. After completion of the reactions, hydrochloric acid was added to remove cobalt carbonyls. In the case of reactions involving alkoxides, this involved acidification of the solution at 0 °C. A bromine water bubbler ensured destruction of hydridotetracarbonylcobalt in the exhaust gases. After stirring for two hours, the absence of cobalt carbonyl species was checked by infrared.

Salts, including anilinium chloride, were removed from the reaction mixtures by means of acid/ether separations. The components of the mixtures, including involatile alcohols, were separated by preparative scale t.l.c. T.l.c. plates were prepared as in the preceding chapter.

N.m.r. spectra were recorded in $CDCl_3$ solution on a Varian T-60

spectrometer, unless otherwise stated. Infrared spectra were recorded in RIIC FH-01 cells on a Perkin-Elmer 577 spectrometer.

Melting points were recorded on a Reichert hot stage microscope and are uncorrected.

General procedure for the formation of hydratropyltetracarbonylcobalt (I) in THF

The required amount of $Co_2(CO)_8$ and the disproportionating catalyst to be used were deposited in the reaction vessel of the apparatus illustrated in figure 20 under one atmosphere of nitrogen. The nitrogen outlet led to another round bottomed three necked flask equipped with a gas inlet, which protruded well into the vessel, a rubber septum cap through which i.r. aliquots could be withdrawn and a gas outlet which led to a series of bubblers containing respectively nujol, bromine water and nujol. The second vessel was cooled to -78 °C throughout the experiment, and periodically analysed for the presence of hydridotetracarbonylcobalt (I).

THF was distilled into the reaction vessel. When valence disproportionation of cobalt carbonyl was complete (typically, about half an hour later), the vessel was purged with carbon monoxide. After a further short period, the calculated quantity of (α-bromoethyl)-benzene was syringed into the flask. The progress of the reaction was monitored by i.r.

General procedure for the formation of hydratropyltetracarbonylcobalt (I) in hydrocarbon solvents

A round bottomed, three necked flask equipped with a rubber

septum cap, a gas inlet and a gas outlet leading through a cold trap was set up and purged with nitrogen. The required amount of $Co_2(CO)_8$ was deposited in the vessel. The disproportionating agent could be added as a solid (together, where necessary, with the solubilising agent) at this stage or, already in solution with the hydrocarbon solvent. In these cases, sufficient tetra-n-butyl-ammonium iodide, or bis-(potassium dicyclohexyl-18-crown-6) tetrabromocobaltate was used to give complete disproportionation of the carbonyl. Sometimes, however, the next step was inaugurated prior to achievement of complete disproportionation.

The required amount of (α-bromoethyl)-benzene was syringed into the vessel, and the formation of the organocobalt intermediate observed by means of infrared spectroscopy.

B) The Reactions

1) The reaction of aniline with benzyl cobalt tetracarbonyl

Apparatus similar to that illustrated in figure 20 was set up. The gas outlet led to a cold trap of design described in section A). The apparatus was purged with nitrogen.

1.083 g Octacarbonyldicobalt and about 2 g dipotassium tetrabromocobaltate were deposited in the reaction vessel. About 50 ml THF was distilled into the flask. When valence disporportionation was complete, the apparatus was purged with CO and 0.5 ml distilled benzyl bromide was added.

The mixture was allowed to react overnight at room temperature . Inspection of the infrared spectrum of the mixture after this time showed that benzyl cobalt tetracarbonyl and phenylacetylcobalt

tetracarbonyl had been formed.

0.8 ml freshly distilled aniline was syringed into the vessel. Although an immediate colour change occurred, infrared spectroscopy indicated that substantially no reaction involving the organocobalt intermediates had taken place. After three days at room temperature, it was found that the intermediates had been destroyed.

Tetracarbonylcobaltate was destroyed by adding hydrochloric acid. An ether/dilute hydrochloric acid separation was carried out and the ether layers dried over $MgSO_4$. The acid layer was made alkaline by adding sodium carbonate. After filtration, to remove precipitated divalent cobalt species, an ether/aqueous base separation was performed. An n.m.r. spectrum of the contents of the ether layer showed these to consist only of aniline. This aniline could be distilled to leave no significant residue.

The non-amine products, a yellow powder, were shown by t.l.c. to contain one major and several minor products. A preparative scale t.l.c. (1 m x 20 cm x 1 mm, distilled methylene chloride eluent) was carried out on 20 % of the solid. 0.1249 g of phenylacetanilide, $PhCH_2CONHPh$, was isolated as a white solid. Recrystallisation from ether gave large white crystals melting at 116 - 117 °C (lit. 116 °C [247]). The yield, based on starting benzyl bromide is 71 %.

2) <u>The production and thermal decomposition of hydratropyltetracarbonylcobalt (I)</u>

Apparatus similar to that described in 1) above was set up. A water condenser was inserted between the reaction flask and its gas

outlet. The assembly was purged with dried, oxygen-free nitrogen.

About 40 ml THF was distilled into the reaction vessel. Some THF was removed by syringe for reference purposes. When the THF reservoir had cooled to room temperature, this and the distillation apparatus were removed and replaced by a simple gas inlet. The apparatus was purged with carbon monoxide, while rapidly stirring to maximise the THF-atmosphere contact.

A brilliant blue solution emerged on adding about 2.5 g dipotassium tetrabromocobaltate. A white solid, presumably potassium bromide, was observed to precipitate.

0.1853 g $Co_2(CO)_8$ was deposited in the vessel. Rapid gas evolution was noted. Over about twelve minutes, the solution reverted from deep green to its original blue colour. An i.r. showed that very little $Co_2(CO)_8$ remained, and that tetracarbonylcobaltate (1-) was the dominant metal carbonyl species.

About two hours thirty minutes after addition of 0.2 ml (α-bromoethyl)-benzene, bands due to an acyl cobalt tetracarbonyl species were found to be present in the infrared spectrum of the mixture.

The mixture was heated to 40 °C. The contents of the cold trap were monitored periodically by i.r. The cold trap was found to contain a small amount of $HCo(CO)_4$ after 2 hours 35 minutes and after 20 hours 30 minutes. The cobalt carbonyl species in the reaction vessel were found to have been destroyed after 22 hours 30 minutes at 40 °C. A weak i.r. absorption was to be seen at 1724 cm^{-1} at this time.

The reaction mixture was allowed to cool to room temperature, acidified, and an ether/aqueous acid separation performed. An analytical t.l.c. indicated the presence of at least fourteen products, two of them giving colouration on spraying with 2,4-dinitrophenylhydrazine. The n.m.r. of the product mixture was immensely complex, but the triplet and quartet due to ethylbenzene could be extricated. A weak, broadened singlet at 9.60 δ indicated that an aldehyde was present.

3) The reaction of hydratropyltetracarbonylcobalt (I) with aniline in THF

Hydratropyltetracarbonylcobalt (I) was formed, by the method described in the general procedure in A) above, from 0.9190 g $Co_2(CO)_8$ and 0.5 ml (α-bromoethyl)-benzene in about 75 ml THF. 4 g K_2CoBr_4 was employed as a disproportionation catalyst.

24 hours after the addition of $PhCH(CH_3)Br$, 4 ml distilled aniline was syringed into the vessel. The colour of the reaction mixture changed immediately from green to blue, but no change was noted in the infrared spectrum of the organocobalt intermediate.

Three days were required for the complete destruction of the organocobalt intermediate.

The non-amine organic products were separated as in A) above. An n.m.r. spectrum showed that hydrocinnamanilide was the major product of the reaction. No evidence of hydratropanilide could be detected. A preparative scale (1 m x 20 cm x 1 mm redistilled methylene chloride eluent) t.l.c., carried out on 50 % of the pale brown solid product mixture showed one major and several minor

components. (One of these minor products gave a positive d.n.p. test.)

0.2190 g $PhCH_2CH_2CONHPh$ melting at 93-95 °C (lit. 97 °C [246]) was collected. This represents a yield of 53 %.

4) The reaction of octacarbonyldicobalt with (α-bromoethyl)-benzene in methanol

A round bottomed, three necked flask provided with a gas inlet, a gas outlet and a rubber septum cap was purged with nitrogen and then with carbon monoxide. 1.5 g K_2CoBr_4 and 0.2383 g $Co_2(CO)_8$ were deposited in the vessel against a counterstream of carbon monoxide. Addition of 40 ml analar methanol gave rise to a deep brown solution. This rapidly evolved gas and changed colour to leave a translucent pink-red solution (within 15 minutes). Inspection of the infrared spectrum of this solution showed that tetracarbonylcobaltate was the only cobalt carbonyl species present.

0.4 ml (α-bromoethyl)-benzene was syringed into the vessel. After stirring for five hours at room temperature, an i.r. spectrum was recorded. This showed the presence of an acyl cobalt intermediate, although a significant quantity of $Co(CO)_4^-$ remained.

A solution of sodium methoxide prepared by adding 0.29 g sodium to 20 ml methanol was added. This immediately destroyed the organocobalt intermediate.

The organic products were separated as in section A). An n.m.r. spectrum showed that $PhCHCH_3CO_2CH_3$ and $PhCHCH_3OCH_3$ had been formed with no evidence of other products. A preparative scale

t.l.c. was carried out on 50 % of the reaction mixture (1 m x 20 cm x 1 mm, redistilled methylene chloride eluent) and 0.1248 g methyl hydratropate was isolated as a colourless liquid. The n.m.r. spectrum of this product was superimposable with that of an authentic sample of the ester. The yield, based on starting (α-bromoethyl)-benzene is 38 %.

5) The reaction of sodium phenoxide with hydratropyltetracarbonylcobalt (I) in toluene

Hydratropyl cobalt tetracarbonyl was formed as in the general procedure outlined in section A). 1.1108 g $Co_2(CO)_8$ and approximately 4 g tetra-n-butylammonium iodide were employed in the formation of the anion. 0.5 ml $PhCHBrCH_3$ was syringed into the vessel, and the mixture stirred at room temperature for four hours.

A solution (suspension?) of sodium phenoxide in toluene was prepared using 0.9590 g phenol and 0.2199 g sodium in 20.0 ml of the solvent. 10.0 ml of this cloudy solution was syringed into the reaction vessel. The progress of the decomposition was monitored by infrared and found to take about 20 hours to go to completion.

The reaction mixture was acidified and worked up as in section A). An analytical t.l.c. showed this to comprise at least ten components. Four of these were positively identified by superimposition of n.m.r.s of authentic samples with an n.m.r. of the product mixture. These were phenol, phenyl 1-phenylethyl ether, phenyl hydratropate and phenyl hydrocinnamate. Comparison of the integral areas of signals from these species showed that phenyl 1-phenylethyl ether and phenyl hydratropate were, by far,

the major products of the reaction.

6) The reaction of sodium tertiary-butoxide with hydratropyltetracarbonylcobalt (I) in THF

Hydratropyltetracarbonylcobalt (I) was prepared by the general method outlined in section A), using 1.0136 g $Co_2(CO)_8$ and 0.5 ml (α-bromoethyl)-benzene in about 75 ml THF in the presence of 2.5 g K_2CoBr_4.

0.406 g sodium was deposited in 20 ml of liquified tertiary butanol. When tertiary butoxide had formed, 10 ml of this solution was transferred to the reaction vessel in a hot syringe.

The progress of the decomposition of the acyl cobalt species was monitored on i.r. After five days, at which time, a little unreacted acylcobalt tetracarbonyl species still remained, HCl was added, and the reaction worked up as in section A).

The reaction mixture was found to contain several products. The major of these was recognised by n.m.r. to be t-butyl hydrocinnamate, presence of a very small amount of t-butyl hydratropate was also detected by superimposition of the n.m.r. spectrum of an authentic sample of the material.

7) The isomerisation of hydratropyltetracarbonylcobalt (I) and subsequent reaction of hydrocinnamyltetracarbonylcobalt (I) with sodium methoxide

Hydratropylcobalt tetracarbonyl was prepared by the general method described in section A), from 0.5121 g $Co_2(CO)_8$ and 0.4 ml (α-bromoethyl) benzene in about 50 ml THF in the presence of about

2 g K_2CoBr_4.

The mixture was stirred for five days at room temperature under one atmosphere of carbon monoxide. Periodically, aliquots were withdrawn for i.r. analysis.

15 ml of a solution of sodium methoxide made up from 0.8 g sodium in 20 ml analar methanol was injected. The reaction mixture became mauve and cloudy. An i.r. aliquot was withdrawn and filtered through a nitrogen-purged cotton wool plug under N_2 pressure. The resultant i.r. showed the presence of tetracarbonylcobaltate as the only cobalt carbonyl species.

The solution was acidified and worked up as in section A). The organic product mixture, a colourless, mobile liquid proved to be mainly composed of methyl hydrocinnamate, as identified by its n.m.r. spectrum.

8) The reaction of the anilide anion with hydratropyltetracarbonylcobalt (I) in THF

Hydratropyltetracarbonylcobalt (I) was prepared from 1.0248 g $Co_2(CO)_8$ and 0.5 ml (α-bromoethyl)-benzene in about 50 ml THF in the presence of 2 g K_2CoBr_4. The method described in section A) was followed.

After eighteen hours, 0.8 ml aniline and 1.7762 g 1,8-bis-(N,N-dimethylamino)-naphthalene were added. About two hours was required for completion of the reaction.

The reaction mixture was acidified and worked up as in section A). An n.m.r. of the product mixture showed that

hydrocinnamanilide and hydratropanilide were present in approximately equal proportions.

A preparative scale t.l.c. (1 m x 20 cm x 1 mm; redistilled methylene chloride eluent) was carried out and $PhCH_2CH_2CONHPh$, 0.2301 g (20 %), M.Pt. 95-96 °C (lit. 97 °C [246]) and $PhCHCH_3CONHPh$, 0.2569 g (31 %), M.Pt. 129-131 °C (lit. 133-134 °C [245]) isolated from adjacent bands.

9) The reaction of aniline with hydratropyltetracarbonylcobalt(I) in benzene

The acyl cobalt tetracarbonyl was formed as in the general method described in section A). 1.0931 g $Co_2(CO)_8$ and 0.5 ml (α-bromoethyl)-benzene were employed in 50 ml benzene. Tetra-n-butylammonium iodide (3 g) was used as the disproportionating agent.

23 Hours after adding the (α-bromoethyl)-benzene, 5 ml aniline was syringed into the vessel. The decomposition of the acyl cobalt tetracarbonyl species was monitored on i.r. After four days at ambient temperature, tetracarbonylcobaltate was found to be the major cobalt carbonyl species.

Hydrochloric acid was added and the reaction mixture worked up as in section A). An n.m.r. spectrum of the mixture showed that hydratropanilide and hydrocinnamanilide had been formed in roughly equal yields. A preparative scale t.l.c. (1 m x 20 cm x 1 mm, methylene chloride eluent) gave 0.1918 g $PhCH_2CH_2CONHPh$ (23 %) M.Pt. 94-96 °C (lit. 97 °C [246]) and 0.1446 g $PhCHCH_3CONHPh$ (18 %) M.Pt. 130-132 °C (lit 133-134 °C [245]). Several minor, unidentified by-products were also formed in the reaction.

CHAPTER FIVE

PERSPECTIVE

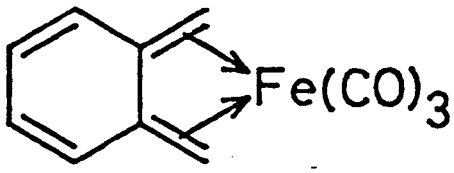
CHAPTER FIVE : PERSPECTIVE

There has been a tendency, over the last two decades, to stress the similarities between the metals in transition metal organic chemistry. The search for general trends has been at least as successful as had been hoped [248]. For example, the same reaction mechanisms have been shown to operate across the transition series [e.g. 159]. In the design of a particular synthesis, however, the unique character of each metal assumes greater importance.

A gross example of this point can be derived from the formation of ketones by iron- and cobalt-carbonyl anions: Tetracarbonylcobaltate (1-) being a monoanion has the ability to form only a monoalkyl derivative. This, as has been shown, decomposes by a binuclear elimination step to yield a symmetrical dialkyl ketone. Tetracarbonylferrate (2-) can react in a stepwise manner with two different alkylating agents. The intermediate so formed decomposes in a mononuclear step to give an unsymmetrical ketone [249].

This work has shown that some expected and some unexpected rearrangements may be suffered by the organocobalt intermediates considered. The rearrangements available to a given alkyl group will depend (as well as on the nature of the alkyl group itself) on the metal to which it is attached. It was shown in chapter three that α, α' - dibromo-o-xylene reacts with tetracarbonylcobaltate (1-) to give an alkyl cobalt tetracarbonyl analogous to benzyltetracarbonylcobalt (I). In contrast, tetracarbonylferrate (2-) reacts with the same dibromide to give

the (diene) iron tricarbonyl species, (XXXIII) [250].



(XXXIII)

This decomposes in the presence of aluminium trichloride to give indan-2-one. The yield of the ketone is substantially lower than that obtained via the cobalt carbonyl intermediate.

Effects such as the above are dependent to a large extent on the periodic group of the metal. It can be readily envisaged that other effects will vary from individual metal to individual metal. The ability to form a metallacycle of a given ring size, and the strength of a given alkyl-metal bond are examples.

The reaction mode adopted by a given metal towards a particular organic compound will depend on such factors as the degree of crowding about the metal, and on the metal's electronic requirements. These points are functions of the metal and of the 'supporting' ligands. Oxidative addition of benzyl halides to tetrakis-(triphenylphosphine)-nickel (0) occurs readily and yields benzyl (halo) bis-(triphenylphosphine)-nickel (II) [251]. On the other hand, dicarbonyl bis-(triphenylphosphine)nickel (0) is relatively unreactive towards benzyl halides. This has been related to the reluctance of dicarbonyl bis-(triphenylphosphine)-nickel (0) to suffer ligand disociation [252].

It is obvious that the study of the effects governing the behaviour of each metal and each metal-ligand system is justifiable.

It has been the intention of this work to assess the viability of tetracarbonylcobaltate (1-) in some simple synthetic steps. Even when considering a single metal, the number of variables is immense. It would be pretentious to claim that this work represents a definitive statement on the above brief. Hopefully, it represents a contribution towards one.

The fortuitous discovery that halides catalyse the valence disproportionation of cobalt carbonyls has allowed reactions of tetracarbonylcobaltate (1-) to be carried out in truly mild conditions. A number of questions have arisen from the study of this reaction: The reaction mechanism is obviously complicated especially in complexing solvents. It has, therefore, been impossible to quantify the factors important in determining the course and rate of the reaction.

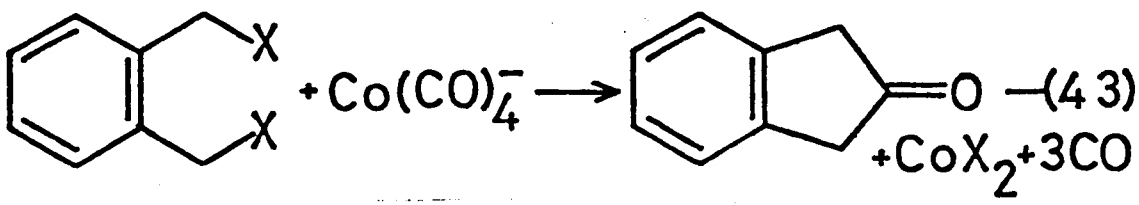
Tetra-n-butylammonium iodide allows convenient conversion of cobalt carbonyls to a soluble salt of tetracarbonylcobaltate and an insoluble divalent cobalt salt in aromatic hydrocarbon solvents. The linear dependence of the rate of this reaction on the concentration of halide (where $[(Bu^n)_4NI] \gg [\text{cobalt carbonyl}]$) offers hope that quantitative conclusions may be drawn about the factors affecting the rate and, ultimately, that the mechanism of valence disproportionation may be elucidated.

The advantages of carrying out synthetic reactions involving tetracarbonylcobaltate in hydrocarbon solvents are 1) that competition between the anion and a basic solvent for an electrophilic substrate is eliminated; 2) that isomerisation of

alkyl- and acyl-cobalt carbonyl intermediates is less ready in hydrocarbons than in more polar (basic?) solvents [222].

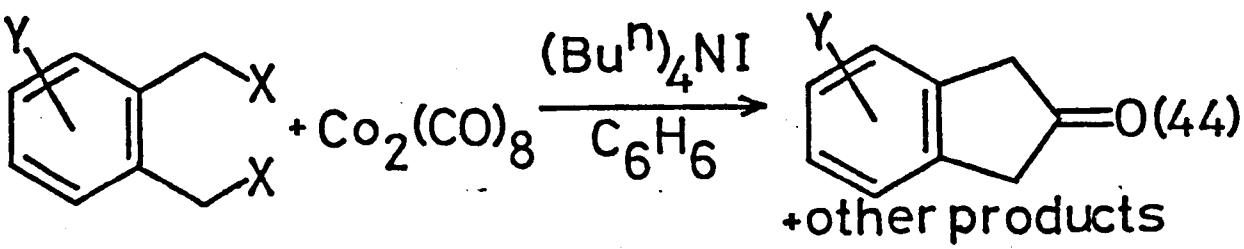
A factor that may transpire to be an advantage of working in benzene is that radical coupling processes proceed with less tendency for radical-solvent reaction in this solvent than in, for example, THF.

The cyclisation reaction, (43), appears to be of limited utility, but the search for cyclisation processes resulting in the production of other ring ketones merits further investigation.



(43)

One obvious case in which the reaction scheme (44) has advantages over conventional means of cyclising α,α'-dihalo-o-arenes (e.g. the Dieckmann cyclisation [253]) is where Y is, or contains, an acid- or base-sensitive functionality.

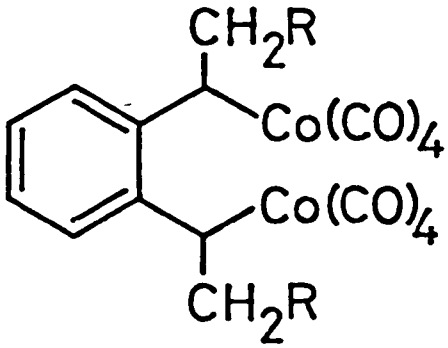


(44)

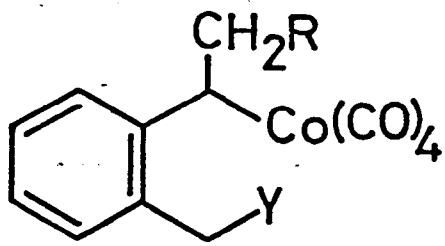
The reaction of aniline with the product of the attack by tetracarbonylcobaltate (1-) on (α-bromoethyl)-benzene under one atmosphere of carbon monoxide does not offer a clean, high yield

method of synthesising the pharmaceutically interesting [254] product, hydratropanilide. By judicious choice of solvent, and by increasing the nucleophilicity of the base, it is possible to increase the yield of the desired, non-isomerised derivative.

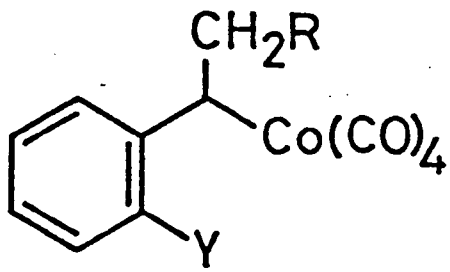
The modes of decomposition of the intermediates (XXXIV), (XXXV) and (XXXVI) should present interesting problems.



(XXXIV)



(XXXV)



(XXXVI)

Y = NHR′ or OH, R = H or alkyl

It is possible that the tendency to isomerise could interfere with, or prevent, the cyclisation reaction in each case. The possibility of the formation of six-membered ring products also exists.

Although the base catalysed alcoholysis and hydrolysis of methylpentacarbonylmanganese (I) have been studied, and shown to

be governed by the same effects as, for example, base hydrolysis of esters [255], the mechanism of the reaction cannot be said to have been fully explored. Since a liaison between phosphorus and cobalt results following attack by phosphines on acyl cobalt tetracarbonyls, it is by no means certain the oxygen- and nitrogen-bases do not attack the acyl group via a transient association with the metal. If this is the case then steric (and electronic) effects at the cobalt, such as the presence of a bulky phosphine ligand, could play a deciding role in determining the amenability of the metal acyl to attack by a particular nucleophile.

All of the syntheses described in this work were performed under (at most) one atmosphere of carbon monoxide. It is expected that the yields of carbonylated and, in many cases, non-isomerised products could be significantly increased by performing the reactions under higher pressures of carbon monoxide.

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